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THE THEORY OF SOME A-C. COMMUTATOR MOTORS WITH SERIES CHARACTERISTICS

III. THE THREE-PHASE SERIES MOTOR[1]

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Abstract

The method previously used in a study of repulsion motors is now applied to the case of the three-phase series motor. This machine, although little used as yet on this continent, has many points of interest. It runs at a high power factor, and its operating characteristics are readily modified by shifting the brushes. As before, the effect of the coils short-circuited by the brushes is studied. Experimental and theoretical results are then compared, and in computing the theoretical performance the effects of short-circuited coils and of saturation are taken into account.

1. Introduction

This motor, invented by Görges in 1891, is shown in its simplest form in Fig. 1. The brush axis of any one phase (such as AO) is displaced through an angle β from the axis aa' of the stator winding. Each phase is therefore equivalent to a simple single-phase series motor, and the direction of the motor torque and of the rotation will be in the direction of brush-shift from the position of exact opposition of stator and rotor; that is, counter-clockwise in the case of Fig. 1.

The motor is therefore equivalent to three single-phase motors super-imposed in such a way that the stator axes are displaced by 120° in time-phase. Owing to this symmetrical three-phase arrangement, however, the operating characteristics differ from those of the single-phase motor in certain ways: (1) The motor torque is constant instead of pulsating; (2) The space-fundamental components of the phase fluxes combine to form a constant "rotating field", rotating at synchronous speed in a direction fixed by the phase-sequence of the supply.

The induced e.m.f's in stator and rotor may be calculated most readily by means of this "rotating field" simile, although of course such e.m.f's are due fundamentally to both rotational and transformer action.

Provided that the direction of rotation of the motor is the same as that of the rotating field, no e.m.f. will be induced in the rotor at synchronism. The inherent commutation should therefore be good at speeds near synchronism,
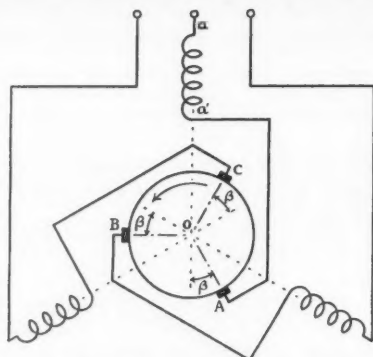
FIG. 1.   *Three-phase series motor.*

but care must be taken to ensure the same direction for rotor and rotating field: the direction of rotation of the rotor depends on the direction of brush-shift and not on the phase sequence, and if the phase sequence is reversed the motor will still operate, but with very poor commutation and power factor.

If a rotor with commutator is driven at speed n and three-phase brushes are supplied with three-phase current at a frequency giving a synchronous speed n_s, the phase-sequence and direction of n being the same, the reactive e.m.f. induced in the rotor winding for a given current will be proportional to $n_s - n$.   That is, the rotor acts as a three-phase load of balanced reactance proportional to $n_s - n$, so that at speeds below synchronism the reactance is positive (inductive) while at speeds above synchronism the reactance is negative (capacitive).   This is the principle of operation of Scherbius phase-advancers, so that the power factor of the motor may be expected to improve as the speed increases, and at some speed above synchronism it should become leading.

If, however, the phase-sequence is reversed, the rotor will have a positive reactance proportional to $n + n_s$, which will continually increase as the speed increases, giving a poor power factor and bad commutation owing to the high e.m.f. induced in the coils short-circuited by the brushes.

In practice, in order to obtain good commutation over a wide range of speed, it is found desirable to make the number of rotor turns considerably smaller than the number of stator turns.   To obtain approximate equality of stator and rotor m.m.f's a three-phase transformer is placed between stator and rotor as in Fig. 2.

In the following theory the presence of the transformer will be ignored, since if all measurements are made on the primary side the results will give effective values referred to the primary, and hence applicable in all equations relating to the primary circuit.   For the high currents taken at low speeds, however, saturation of the transformer may complicate matters owing to the increase in magnetizing current.
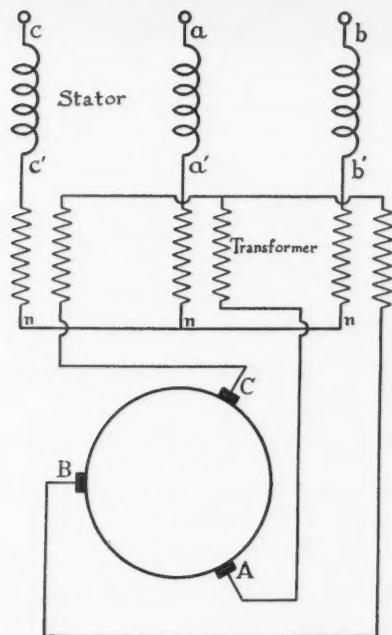
FIG. 2. *Three-phase series motor with inter-winding transformer.*

2. Theory Neglecting the Effect of Short-circuited Coils

Consider the e.m.f's induced in phase a. Let A represent the resultant rotating m.m.f. due to all three phases, its components being A_1 and A_2 due to the stator and rotor currents respectively. The rotating m.m.f. A_1 will be directed along the stator axis of phase a when the current in that phase is a maximum, and at the same instant A_2 will be directed along the brush axis AO (Fig. 1). The relations between A, A_1, and A_2 at this instant are shown in Fig. 3. As before, the flux ϕ and its components ϕ_1 and ϕ_2 may be taken as being approximately in-phase with the m.m.f.'s.

The total stator flux, $\phi_1 + \phi_{L_1}$, will induce an e.m.f. in the stator:

$$E_{s1} = -jIX_1. \tag{1}$$

The rotor-component of mutual flux, ϕ_2, will induce an e.m.f. in the stator which will lag behind E_{s1} by the phase angle $\pi - \beta$, so that

$$E_{s2} = -jIX_{12}e^{-j(\pi-\beta)} = -IX_{12}(\sin\beta - j\cos\beta). \tag{2}$$

The total stator e.m.f. is therefore

$$E_s = E_{s1} + E_{s2} = -I[X_{12}\sin\beta + j(X_1 - X_{12}\cos\beta)]. \tag{3}$$

The flux component ϕ_1 will have its maximum linkage with the rotor phase at an angle $\pi + \beta$ later than the instant of its maximum linkage with the
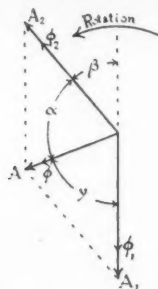
FIG. 3.   *Components of magnetomotive force.*

stator.   Thus, since its speed is $n_s - n$ relative to the rotor, it induces a rotor
e.m.f. per phase:

$$E_{r1} = -jQ_2(n_s - n)\phi_1 e^{-j(\pi + \beta)} = IX_{12}\left(1 - \frac{n}{n_s}\right)(\sin \beta + j \cos \beta). \quad (4)$$

The total rotor-component of flux, $\phi_2 + \phi_{L2}$, will induce an e.m.f. in the rotor
which will be in-phase with E_{s1}, so that

$$E_{r2} = -jIX_2\left(1 - \frac{n}{n_s}\right). \quad (5)$$

(This is the "reactance e.m.f." of the rotor of a Scherbius phase-advancer.)
The total rotor e.m.f. is then

$$E_r = E_{r1} + E_{r2} = I\left(1 - \frac{n}{n_s}\right)[X_{12} \sin \beta - j(X_2 - X_{12} \cos \beta)]. \quad (6)$$

The terminal p.d. per phase is

$$V = -E_s - E_r + IR, \quad (7)$$

where R is the effective resistance per phase of the motor and is given by

$$R = R_1 + r_1 + a_t^2(R_2 + r_2), \quad (8)$$

where R_1 = resistance of stator phase; R_2 = resistance of rotor phase; r_1 =
resistance of transformer primary, per phase; r_2 = resistance of transformer
secondary, per phase, and a_t = transformer ratio.

The p.d. across a stator phase is $V_s = -E_s + IR_1$, or

$$V_s = I[R_1 + X_{12} \sin \beta + j(X_1 - X_{12} \cos \beta)]. \quad (9)$$

The p.d. across the transformer primary is

$$V_t = -E_r + (R - R_1) I$$
$$= I\left[R - R_1 - \left(1 - \frac{n}{n_s}\right)X_{12} \sin \beta + j(X_2 - X_{12} \cos \beta)\right], \quad (10)$$

and the terminal p.d. is $V = IZ_{et}$, where

$$Z_{et} = \left(R + \frac{n}{n_s} X_{12} \sin \beta\right)$$
$$+ j\left\{(X_1 + X_2 - 2X_{12} \cos \beta) - \frac{n}{n_s}(X_2 - X_{12} \cos \beta)\right\}. \quad (11)$$

The second half of the j-term is the cause of the high or leading power factor at high speeds.

FIG. 4.   *Vector diagram, three-phase series motor.*

The vector diagram per phase is shown in Fig. 4, from which it is seen that the angle ψ is given by

$$\tan \psi = \frac{X_2 - X_{12} \cos \beta}{X_{12} \sin \beta} .$$ (12)

The gross motor power is

$$P_m = I^2 \frac{n}{n_s} X_{12} \sin \beta.$$ (13)

The gross torque is

$$T = 0.117 \frac{P_m}{n} \text{ lb. ft.}$$ (14)

The minimum stable speed

It is seen from the vector diagram that the equivalent impedance, Z_{et}, is not necessarily a minimum at standstill. The minimum value, and hence the maximum value of the gross torque, will occur at a finite speed n_0 such that the vector V is perpendicular to the vector XA (Fig. 4). This condition, which gives maximum current for a given p.d., gives the minimum speed, n_0, at which the motor will operate stably. We have, in Fig. 4:

$$XA = XB - AB = XR \sin \psi - OR \cos \psi,$$

whence

$$XA^2 = \frac{n_0}{n_s} \{(X_1 + X_2 - 2X_{12} \cos \beta)(X_2 - X_{12} \cos \beta) - RX_{12} \sin \beta\} ,$$

which gives for the speed n_0 :

$$\frac{n_0}{n_s} = \frac{(X_2 - X_{12} \cos \beta)(X_1 + X_2 - 2X_{12} \cos \beta) - RX_{12} \sin \beta}{X_{12}^2 \sin^2 \beta + (X_2 - X_{12} \cos \beta)^2} ,$$ (15)

which shows that under certain conditions, for a particular brush angle, the maximum torque can occur at starting. If resistance is neglected, this condition is given by $X_2 = X_{12} \cos \beta$.

The determination of n_0 can, of course, be performed graphically instead of by the use of Equation (15).

As a further approximation, let us neglect leakage and assume the stator and rotor winding factors to be equal. We may then put $X_1 = cN_1^2$, $X_2 =$

cN_2^2, $X_{12} = cN_1N_2$, whence Equation (15) reduces to

$$\frac{n_0}{n_s} \doteq 1 - \frac{N_1}{N_2}\cos\beta \,, \tag{16}$$

a result given by Rüdenberg for an "ideal" motor (5, p. 233).

Effect of transformer ratio

If N_2 in Equation (16) is the actual number of rotor turns, and the transformer ratio is a_t, then the speed n_0 is, for the same approximations, given by

$$\frac{n_0}{n_s} \doteq 1 - \frac{N_1}{a_tN_2}\cos\beta. \tag{17}$$

The value of the maximum torque, neglecting resistances

Putting $n/n_s = n_0/n_s$ in Equation (11), we find for the value of Z_{et} at the minimum stable speed, when resistance is neglected:

$$(Z_{et0})^2 \doteq \frac{(X_{12}\sin\beta)^2(X_1 + X_2 - 2X_{12}\cos\beta)^2}{X_{12}^2\sin^2\beta + (X_2 - X_{12}\cos\beta)^2} \,, \tag{18}$$

whence, putting $I^2 = (V/Z_{et})^2$ in Equation (14), we find

$$T_{max} \doteq \frac{0.117\ I^2}{n_s}\ \frac{(X_2^2 - 2X_2X_{12}\cos\beta + X_{12}^2)}{X_{12}\sin\beta\ (X_1 + X_2 - 2X_{12}\cos\beta)^2} \,. \tag{19}$$

The starting torque

Neglecting resistances, we have $(Z_{et})_{n=0} = X_1 + X_2 - 2X_{12}\cos\beta$, so that

$$T_S \doteq \frac{0.117\ I^2}{n_s}\ \frac{X_{12}\sin\beta}{(X_1 + X_2 - 2X_{12}\cos\beta)^2} \,. \tag{20}$$

The ratio

$$\frac{\text{Maximum torque}}{\text{Starting torque}} \doteq 1 + \left(\frac{X_2 - X_{12}\cos\beta}{X_{12}\sin\beta}\right)^2 \,. \tag{21}$$

Thus the maximum torque can occur at standstill only if $X_2 \doteqdot X_{12}\cos\beta$.

3. The Effect of the Currents in the Short-circuited Coils

The positive direction of the e.m.f's induced in the coil short-circuited by the brush A is shown by the dotted and crossed conductors in Fig. 5. It is such that it will cause a current having a m.m.f. in the direction m_s. The e.m.f. induced in the short-circuited coil is found as follows.

The flux-component ϕ_1 will have its maximum linkage with the shorted coil at an instant $\pi/2 + \beta$ later than with the stator phase. The e.m.f. in the coil due to ϕ_1 is therefore

$$e_{c_1} = -jQ_s(n_s - n)\phi_1e^{-j\left(\frac{\pi}{2} + \beta\right)}$$

$$= -IX_{sm_1}\left(1 - \frac{n}{n_s}\right)(\cos\beta - j\sin\beta), \tag{22}$$

where X_{sm1} is equal to the flux-linkages per ampere with the shorted coil due to the stator flux ϕ_1 of all three phases.
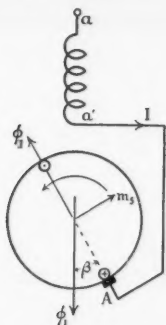
FIG. 5. *Direction of e.m.f's in a coil short-circuited by a brush.*

The flux ϕ_2 will have its maximum linkage at an angle $\alpha + y = \pi - \beta$ later than the flux ϕ_1; that is, $\pi/2 + \beta + \pi - \beta = 3\pi/2$ later than the instant of maximum linkage of ϕ_1 with the stator phase. It will therefore induce an e.m.f. in the coil:

$$e_{c_2} = -jQ_s(n_s - n)\phi_2 e^{-j3\pi/2} = IX_{sm_2}\left(1 - \frac{n}{n_s}\right). \tag{23}$$

For simplicity, assume $X_{sm1} \doteqdot X_{sm2} = X_{sm}$; then the total e.m.f. in the shorted coil is

$$e_c = IX_{sm}\left(1 - \frac{n}{n_s}\right)(1 - \cos\beta + j\sin\beta). \tag{24}$$

The current in the shorted coil, due to e_c, is $I_c = e_c/(R_s + jX_s)$, where X_s, the reactance of the shorted coils of one phase considered as one coil, must include the mutual reactances with the shorted coils of the other two phases. Then

$$I_c = \frac{IX_{sm}(1 - n/n_s)}{Z_s^2}$$

$$[\{R_s(1 - \cos\beta) + X_s\sin\beta\} + j\{R_s\sin\beta - X_s(1 - \cos\beta)\}]. \tag{25}$$

This current combines with similar currents in the coils shorted by the brushes of the other two phases to set up a field rotating at speed n_s relative to the stator. This field has its maximum linkage (in the positive direction) with the stator phase a at an angle $3\pi/2 - \beta$ later than the instant of maximum current. The e.m.f. induced in the stator is therefore

$$E_{sc} = -jI_cX_{sm}e^{-j(3\pi/2-\beta)} = jI_cX_{sm}(\sin\beta - j\cos\beta). \tag{26}$$

Substituting for I_c from Equation (25) we get

$$E_{sc} = -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)$$

$$[R_s(1 - \cos\beta) - X_s\sin\beta - j\{R_s\sin\beta + X_s(1 - \cos\beta)\}]. \tag{27}$$

The rotating field of the short-circuit currents will have its maximum linkage with the rotor phase $\pi - \beta$ *earlier* than with the stator phase; that is, $\pi/2$

later than the instant of maximum current.   The transformer e.m.f. induced in the rotor is then:

$$E_{rc} = -jI_cX_{sm}e^{-j\pi/2} = -I_cX_{sm} = -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)$$
$$[R_s(1 - \cos\beta) + X_s\sin\beta + j\{R_s\sin\beta - X_s(1 - \cos\beta)\}] . \quad (28)$$

As in the case of the repulsion motor, the corresponding rotational e.m.f. in the rotor is neglected.   The total e.m.f. induced per phase by the short-circuit currents is therefore

$$E_c = E_{sc} + E_{rc} = -2I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)(1 - \cos\beta)(R_s - jX_s). \quad (29)$$

The terminal p.d. is increased by $-E_c$.   The equivalent *total* impedance of the motor is increased by

$$Z' = (1 - \cos\beta)\left(1 - \frac{n}{n_s}\right)(R_c - jX_c), \quad (30)$$

where

$$R_c = 2R_s\left(\frac{X_{sm}}{Z_s}\right)^2 \quad \text{and} \quad X_c = 2X_s\left(\frac{X_{sm}}{Z_s}\right)^2 . \quad (31)$$

The input per phase is increased by

$$I^2R_c(1 - \cos\beta)\left(1 - \frac{n}{n_s}\right). \quad (32)$$

The copper loss in the shorted coil (per phase) is

$$I_c^2R_s = \frac{e_c^2}{Z_s^2}R_s = I^2R_c(1 - \cos\beta)\left(1 - \frac{n}{n_s}\right)^2. \quad (33)$$

The gross power is increased by

$$P_{mc} = I^2R_c(1 - \cos\beta)\left(1 - \frac{n}{n_s}\right) - I_c^2R_s$$
$$= I^2R_c\frac{n}{n_s}\left(1 - \frac{n}{n_s}\right)(1 - \cos\beta), \quad (34)$$

which is zero both at standstill and synchronism.

The gross torque, per phase, is increased by

$$T_c = 0.117\frac{P_{mc}}{n} . \quad (35)$$

The equivalent true resistance (giving the total copper losses), per phase, now becomes:

$$R_e' = R + R_c(1 - \cos B)\left(1 - \frac{n}{n_s}\right)^2. \quad (36)$$

The equivalent standstill reactance is

$$X_e' = X_1 + X_2 - 2X_{12}\cos\beta - X_c(1 - \cos\beta). \quad (37)$$

The component of p.d. which cancels the rotational e.m.f. now becomes

$$-E_r = I\frac{n}{n_s}[X_{12}\sin\beta - j(X_2 - X_{12}\cos\beta) - (1 - \cos\beta)(R_c - jX_c)]. \quad (38)$$

The total equivalent impedance is

$$Z'_{et} = R + R_c(1 - \cos\beta) + \frac{n}{n_s}\{X_{12}\sin\beta - R_c(1 - \cos\beta)\}$$
$$+ j\left[X_1 + X_2 - 2X_{12}\cos\beta - X_c(1 - \cos\beta)\right. \tag{39}$$
$$\left. - \frac{n}{n_s}\{X_2 - X_{12}\cos\beta - X_c(1 - \cos\beta)\}\right].$$

The gross motor power becomes

$$P_m' = P_m + P_{mc} = I^2\frac{n}{n_s}\left[X_{12}\sin\beta + R_c(1 - \cos\beta)\left(1 - \frac{n}{n_s}\right)\right]. \tag{40}$$

The starting torque. Neglecting resistances, this becomes

$$T_S' = \frac{0.117\ V^2}{n_s}\frac{X_{12}\sin\beta}{\{X_1 + X_2 - 2X_{12}\cos\beta - X_c(1 - \cos\beta)\}^2}. \tag{41}$$

The vector diagram

The vector diagram, when the effect of the shorted coils is included, is shown in Fig. 6, which should be compared with Fig. 4.
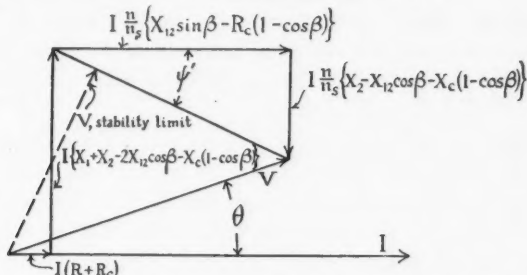

FIG. 6. *Vector diagram, three-phase series motor, allowing for the effect of the short-circuited coils.*

It is seen that the angle ψ' is given by

$$\tan\psi' = \frac{X_2 - X_{12}\cos\beta - X_c(1 - \cos\beta)}{X_{12}\sin\beta - R_c(1 - \cos\beta)}. \tag{42}$$

4. The Current Locus for Constant Reactances

The current loci, with and without the correction for the short-circuit currents, are circles that intersect at the origin and at the point corresponding to synchronous speed. The circles are shown in Fig. 7; the construction is as follows:

Uncorrected for effect of shorted coils	Corrected for effect of shorted coils
$OX = X_1 + X_2 - 2X_{12}\cos\beta$	$OX' = OX - X_c(1 - \cos\beta)$
$XR = R$	$X'R' = XR + R_c(1 - \cos\beta)$
$\tan\psi = \dfrac{X_2 - X_{12}\cos\beta}{X_{12}\sin\beta}$	$\tan\psi'$ given by Equation (42).

The uncorrected current locus is the inverse of the line RN with respect to the origin O. It is a circle, centre C, passing through the origin.

The corrected current locus is the inverse of the line $R'N'$ with respect to the origin O. It is a circle, centre C', passing through the origin.
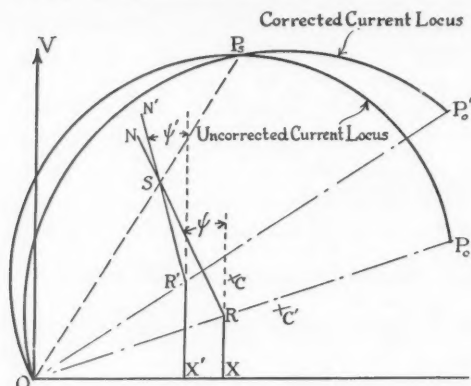
FIG. 7.   *Three-phase series motor, circle diagrams.*

The two circles intersect at the point P_s, which represents synchronous speed.   Further, the lines RN and $R'N'$ intersect at S, corresponding to the impedance vector at synchronous speed. RN and $R'N'$ can be calibrated as speed scales.

It is seen that at standstill (P_0 and P_0') the corrected circle gives a higher current, power, and power factor than the uncorrected case.   Except at synchronous speed, for a given power input the effect of the shorted coils is to increase the current and reduce the power factor.   The maximum possible power input is also reduced.

5. Measurement of the Reactances

(A) R_c and X_c

Let the rotor be open-circuited and ordinary impedance measurements made on the stator.   Then the flux ϕ_1 induces an e.m.f. in the short-circuited coil equal to e_{c1} (Equation (22)).   The flux ϕ_2 is absent so that the current induced in the coil is

$$I_c = \frac{e_{c1}}{R_s + jX_s}$$

$$= -I\frac{X_{sm}\left(1 - \dfrac{n}{n_s}\right)}{Z_s^2}\,[R_s\cos\beta + X_s\sin\beta + j(X_s\cos\beta - R_s\sin\beta)].$$

This current induces an e.m.f. in the stator

$$E_s = jI_cX_{sm}(\sin\beta - j\cos\beta),\text{ as before,}$$

$$= -I\left(\frac{X_{sm}}{Z_s}\right)^2\left(1 - \frac{n}{n_s}\right)(R_s - jX_s), \tag{43}$$

which is independent of β.   That is, the position of the brushes in this test is immaterial.

Thus at *standstill*, the apparent reactance of the stator is *decreased by*

$$X_s \left(\frac{X_{sm}}{Z_s} \right)^2 = \tfrac{1}{2} X_c, \tag{44}$$

and the apparent resistance in *increased* by

$$R_s \left(\frac{X_{sm}}{Z_s} \right)^2 = \tfrac{1}{2} R_c. \tag{45}$$

(B) Stator reactance, X_1

With reference to Fig. 2, a', b', and c' are disconnected from the transformer and joined together in a star point. The brushes are lifted. Measurements are then made with a balanced variable three-phase supply at the stator terminals a–b–c, for a current varying from a low value up to about rated load current.

If I, V, W, and R are per-phase values, X_1 is given by Equation 49†*, or approximately by Equation 48†. If the test is repeated with the brushes down, X_c may be obtained from Equation (44).

The mutual reactance, X_{12}

This may be found in three ways.

(a) Stator to rotor. The stator winding is connected as for the measurement of X_1. The brushes are left down and, in addition to stator amperes, volts, and watts (I, V, W), the rotor phase volts, V_2, are measured across
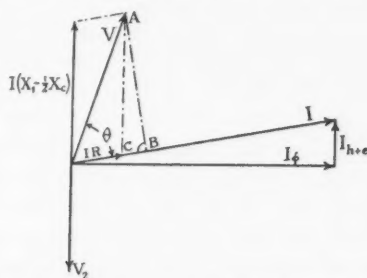
FIG. 8.   *Vector diagram showing the effect of core loss.*

the open-circuited primary of the transformer $a'n$. $(X_{12} - \tfrac{1}{2} X_c)$ is given roughly by V_2/I, but to allow for the stator resistance and core loss angle we have, from the vector diagram shown in Fig. 8:

$$X_{12} - \tfrac{1}{2} X_c = \frac{V_2}{I_\phi} = \frac{V_2 I}{I\, I_\phi} = \frac{V_2 \cdot AC}{I \cdot AB} = \frac{V_2 I (X_1 - \tfrac{1}{2} X_c)}{I\, V \sin \theta}$$

$$= \frac{V_2}{I} \sqrt{\frac{V^2 + I^2 R^2 - 2WR}{V^2 - W^2/I^2}}. \tag{46}$$

From the same test we obtain $X_1 - \tfrac{1}{2} X_c$, and hence X_c.

* *In this paper, a dagger (†) following an equation number indicates that the equation is the one bearing that number in Part I of this series (2).*

(b) Rotor to stator. The connections are the same as in *(a)* except that three-phase power is supplied to the primary of the transformer, and the voltage V_2 in Equation (46) is that across the open-circuited stator, aa'.

The two values of X_{12} so obtained should be found to give a reasonable check. They can be plotted on a base of I and a mean value taken in calculations.

(c) From the equivalent leakage reactance, x_e. If x_e is determined by short-circuit tests, X_{12} may be found by means of Equation 6†. This is found in practice to be the most satisfactory method.

The rotor reactance (referred to stator), X_2

The readings V, I, W on the primary side of the transformer in test *(b)* for X_{12} will give:

$$X_2 + X_t - \tfrac{1}{2}X_e = \frac{\sqrt{V^2 + I^2R^2 - 2WR}}{I}, \qquad (47)$$

where X_t is the equivalent leakage reactance of the transformer and is found in the usual manner. Whence, knowing X_e, X_2 is found and plotted on a base of I.

Determination of the reactances under running conditions

If at any particular speed we measure *(a)* supply volts, amperes, and watts, *(b)* p.d. across a stator phase, and *(c)* p.d. across the transformer primary, we may determine X_1, X_2, and X_{12} (neglecting the effect of the shorted coils). For from *(a)* we can calculate Z_{e1}, and Equations (9), (10), and (11) are sufficient to find the three reactances and the resistance $R - R_1$, while R_1 can be measured directly. The equations reduce to their simplest form at synchronous speed.

The effective resistance, R

The resistance R is given by Equation (8), where R_1, r_1, and r_2 are constant but R_2 includes the variable brush-contact resistance. Hence for accurate results R must be taken, like the reactances, as a function of the current I.

From the results of the test for X_2 we may obtain an equivalent resistance $R_e = W/I^2$ which, in addition to $r_1 + a^2(R_2 + r_2)$, includes $\tfrac{1}{2}R_c$ and also a fictitious resistance r_c such that I^2r_c is equal to the core loss. The core loss, for a given current, is a maximum at standstill and is difficult to calculate at a given speed. Hence we shall be on the safe side if we include its effect in R_e thus obtained. The total effective resistance per phase is then given by

$$R = R_1 + R_e \qquad (48)$$

which can be plotted as a function of I, and in which $\tfrac{1}{2}R_c$ appears as a rough approximation for $R_c(1 - \cos \beta)$.

6. The Effect of Saturation

In Fig. 3 put $A_2 = A_1/a$, where a is the equivalent turns ratio, stator to rotor, and is given by

$$a = \frac{N_1k_1}{a_t N_2k_2}; \qquad (49)$$

then $A = yA_1$, where

$$y = \frac{\sqrt{1 - 2a \cos \beta + a^2}}{a} . \tag{50}$$

If $a = 1$, this reduces to

$$y = 2 \sin \frac{\beta}{2} . \tag{51}$$

If the motor current is I, then the flux-density is produced by the m.m.f. $A = yA_1$. The measured values of X_1, X_2, and X_{12} are found, and plotted, as functions of I, under conditions in which the stator and rotor m.m.f's act separately. Since the resultant magnetizing current under running conditions is yI, the values of X_1, etc., for a motor current I are those that correspond to a current $I' = yI$ on the graphs of X on I.

7. Experimental Results for a Three-phase Series Motor

The motor was a 3-phase Oerlikon machine with inter-winding transformer, 4-pole, 60 cycles, 220 volts, 4.5–8 h.p., in the Electrical Engineering Laboratory of the University of British Columbia.

Winding data

  Stator: 48 slots; 15 conductors in series per slot; star-connected; $k_1 = 0.957$; conductors in series per pole per phase $= Z_1 = 60$.

  Rotor: 42 slots; 6 conductors in series per slot; delta connected; $k_2 = 0.957$.

  Commutator: 126 segments; one turn per segment. One brush set per phase per pair of poles. Each brush shorts two turns most of the time. That is, two conductors in series per pole per phase are shorted by the brushes. The actual conductors in series per pole per phase $= 21$.

  Effective conductors per pole per phase $= 21 - 2 = 19$. Effective conductors per pole per phase, equivalent star connection, $= Z_2 = 19/\sqrt{3}$ $= 10.95$.

Transformer ratio: $a_t = 5.6$.

Transformer leakage reactance: $X_t = 0.07$.

Stator/rotor equivalent turns ratio:

$$a = \frac{Z_1 k_1}{a_t Z_2 k_2} = \frac{60}{5.6 \times 10.95} = 0.98 \doteq \text{unity.}$$

The reactances, etc., were determined as outlined in Sections 1–6. Fig. 9 shows values of : $(a) X_1$, $(b) X_1 - \frac{1}{2}X_e$, $(c) X_2 + X_t - \frac{1}{2}X_e$, $(d) X_{12} - \frac{1}{2}X_e$, all plotted on a base of resultant magnetizing current I'. Curve (d) is plotted from the mean of two tests, stator to rotor and rotor to stator. Fig. 10 shows values of X_e, the equivalent leakage reactance, and R, the effective resistance, which are functions of the actual current I.

The method of calculation of the speed and power factor for an arbitrary current is illustrated by the following example.

$\beta = 30°$. Current $I = 17.8$ amp. $y = 2 \sin \frac{1}{2}\beta = 0.518$. $I' = yI = 9.22$.

$X_1 = 10.81$, $X_1 - \frac{1}{2}X_c = 8.72$; $X_2 + X_t - \frac{1}{2}X_c = 8.75$; $R = 1.25$,

so that

$$X_c = 4.18, \quad X_2 = 10.77.$$

$$X_e = 0.90, \quad X_{12} = \sqrt{X_1 X_2} - \frac{1}{2}X_e = 10.34.$$
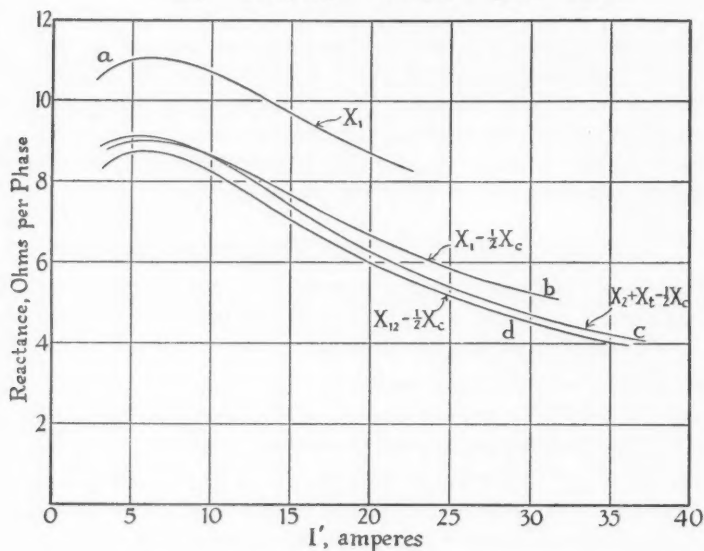

FIG. 9.   *Reactance curves of three-phase series motor.*
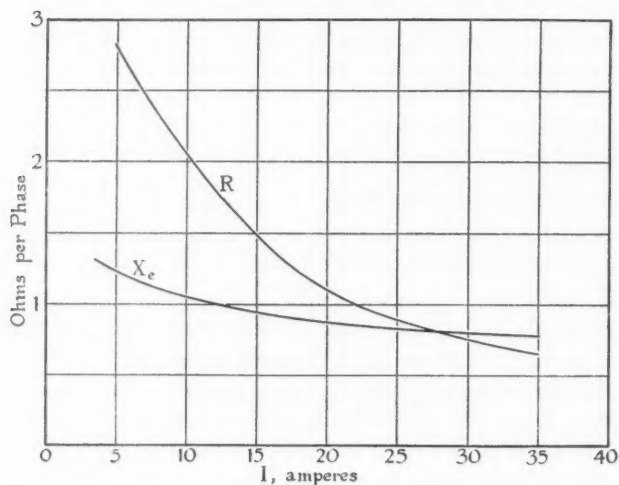
FIG. 10.   *Three-phase series motor.   Total effective resistance and leakage reactance*

Whence, from Equation (39)

$$Z'_{et} = \left(1.25 + 5.17\frac{n}{n_s}\right) + j\left(3.180 - 1.255\frac{n}{n_s}\right) = \frac{220}{\sqrt{3} \times 17.8} = 7.135 \text{ ohms}$$

(scalar value), which gives the quadratic:

$$28.304\left(\frac{n}{n_s}\right)^2 + 4.943\frac{n}{n_s} - 39.233 = 0,$$

whence

$$\frac{n}{n_s} = 1.093, \quad \text{and} \quad n = 1.093 \times 1800 = 1967 \text{ r.p.m.}$$

(cf. 2090 r.p.m. measured)

The power factor

We have

$$R'_{et} = 1.25 + 1.093 \times 5.17 = 6.901,$$

$$\cos\theta = R'_{et}/Z'_{et} = 6.901/7.135 = 0.967 \text{ (cf. 0.968 measured).}$$

The calculated results are compared with experimental values for $\beta = 30°$, $40°$, and $50°$ in Figs. 11 and 12.

On the whole, the correspondence is good. The disturbing factors which have not been taken into account are: (a) the variation of R_e with *speed*, owing to variation of core loss. R_e was measured under conditions of high core loss (standstill) so that one would expect the error due to this cause to be greatest near synchronous speed, and to decrease as the speed deviates from synchronism. This tendency is shown in the curves of Figs. 11 and 12.
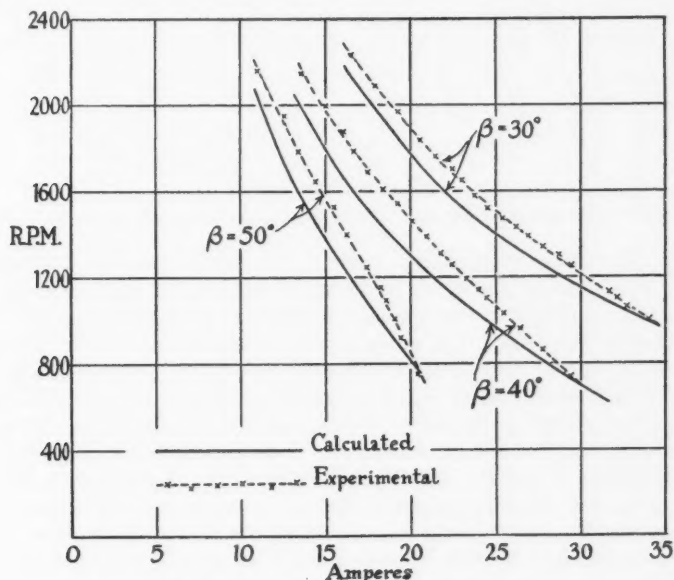
FIG. 11. *Results for three-phase series motor.*
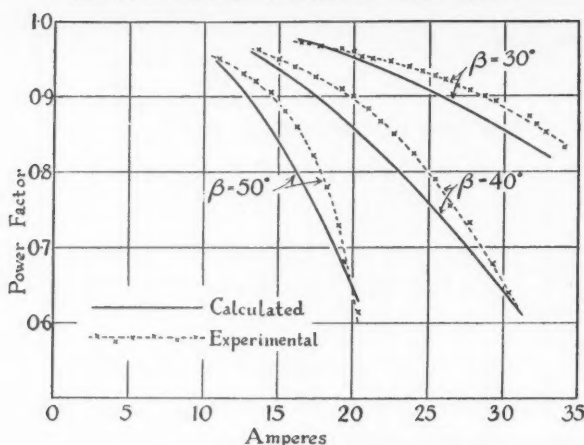
FIG. 12.   *Results for three-phase series motor.*
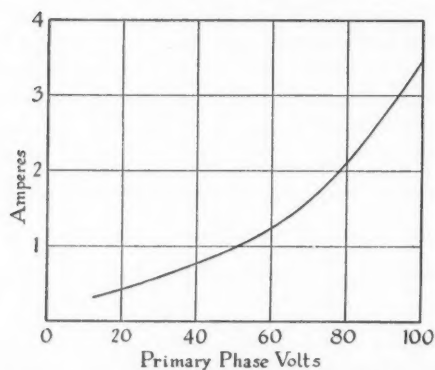
FIG. 13.   *Three-phase series motor.   Magnetizing current of inter-winding transformer.*

(b) The effect of the magnetizing current of the transformer: the magnetizing current flows through the stator of the motor but not through the rotor, and hence causes an error in the assumption that the equivalent current is the same in both windings.   The magnetizing current is shown in Fig. 13 as a function of the p.d. across the transformer primary.   This effect will be a minimum near synchronism, and is difficult to calculate since it will depend on the phase of the magnetizing current and this will vary with the speed. (c) For values of $\beta < 60°$, R_e is too large since it includes $\frac{1}{2}R_e$ as an approximation to $R_e (1 - \cos \beta)$.   (d) When both windings carry current, the ratio of X_{12} to X_1 and X_2 will be slightly different from the values obtained when only one winding is energized, since both stator and rotor teeth will have normal saturation.   (e) The rotational e.m.f. caused by the currents I_e has been neglected.

Acknowledgments

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THE HYDROLYSIS OF PROPIONITRILE IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS[1]

BY B. S. RABINOVITCH[2], C. A. WINKLER[3], AND A. R. P. STEWART[4]

Abstract

The hydrolysis of propionitrile has been studied in aqueous hydrochloric acid solutions from 0.5 to 10 N and over a range of temperatures at six acid concentrations. The rate of hydrolysis as measured by ammonia formation is dependent upon the decomposition of the intermediate amide at acid concentrations above 4 N. The system represented by nitrile $\xrightarrow{k_1}$ amide $\xrightarrow{k_2}$ acid affords a good example of consecutive, irreversible unimolecular reactions over the complete range $k_1 \ll k_2$ (below 4 N) to $k_1 \gg k_2$ (above 11 N). A marked increase in rate with increasing acid concentration is accounted for in large measure by a decrease in observed activation energy of 6.7 Cal. over the range 1 to 10 N.

Introduction

A recent communication (19) from this laboratory on the hydrolysis of amides in concentrated hydrochloric acid solutions has emphasized the importance of determining the parameters of the Arrhenius equation over the entire range of acid concentrations used. It seemed of particular interest to extend the investigation of the Arrhenius constants for reactions in concentrated acid solutions to the hydrolysis of aliphatic nitriles. This reaction has rate characteristics which differ from those for amide hydrolysis. The rate of nitrile hydrolysis increases more rapidly with increase of acid concentration than any other reaction studied in concentrated acid solution (11), whereas that of amide hydrolysis, as measured by the unimolecular constants, passes through a maximum value at around 3 to 6 N acid (10). Furthermore, relatively few data on activation energies for nitrile hydrolysis are available.

The hydrolysis of nitriles proceeds through the amide to yield ammonia and the corresponding acid, according to the equation:

$$RCN \xrightarrow{H_2O} RCONH_2 \xrightarrow{H_2O} RCOOH + NH_3$$
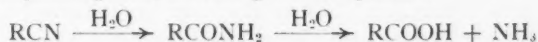
The rate of reaction for simple aliphatic nitriles is generally regarded as being much slower than the rate of amide hydrolysis. In a recent paper, Krieble and Noll (11) have assumed that this rate relation is maintained up to hydro-

chloric acid concentrations of the order 8 to 14 molal. They suggest that at
still higher concentrations the rate of reaction, as measured by ammonia
production, may no longer be independent of the hydrolysis of the intermediate
amide. However, in view of the different way in which the rates of the two
reactions are influenced by acid concentration, it appeared that the rate
of nitrile hydrolysis should be comparable with that of amide hydrolysis at
concentrations below the maximum used by Krieble and Noll. This supposi-
tion was supported by comparison of the rate data for amides obtained in the
previous study (19) with their values for nitriles.

Since there was some uncertainty about the part played by hydrolysis of
the intermediate amide in nitrile hydrolysis, it was obviously necessary to
clarify this point before investigating the Arrhenius equation for a number of
nitriles. This question has therefore been investigated during a study of the
Arrhenius constants for the hydrolysis of propionitrile by hydrochloric acid,
over a range of concentrations from 0.5 to 10 N.

Materials and Procedure

Propionitrile was obtained commercially and was purified to a boiling range
of 0.2° C. on a column of the Whitmore type. Aqueous solutions of the nitrile
were made by weight to give a concentration in the reaction mixtures of
approximately 0.2 N.

Acid solutions were prepared by dilution of reagent grade, concentrated
hydrochloric acid, previously standardized by density measurements and
titration.

At acid concentrations other than 10 N, reaction mixtures of desired com-
position were prepared by mixing appropriate volumes of nitrile and acid
solutions at 0° C. Concentrations after mixing were calculated from the
density–percentage data for hydrochloric acid in International Critical Tables.
Since the nitrile solutions were dilute, they were treated as pure water in these
calculations. Small Pyrex tubes, filled so as to leave little dead space, were
sealed and immersed in thermostats regulated to within 0.1° C. Temperature
was measured with standard thermometers. An experimentally determined
correction was applied for the time required for the solutions to come to
reaction temperature. The duration of even the shortest runs exceeded an
hour. At acid concentration of 10 N, where the reaction temperatures were
lower, the solutions were brought to temperature prior to mixing in a stop-
pered, glass reaction vessel.

The rate of production of ammonia alone was followed by Folin's aspiration
method (3), calibrated and applied at 0° C. in a standard manner. Experi-
ments with standard propionamide solutions showed that a constant fraction
of 2% of the amide present was converted to ammonia during analysis. No
correction was considered necessary for the present purposes. Blank experi-
ments showed no hydrolysis of nitrile under these conditions.

Total amide and ammonia were determined by a modified technique. The
alkaline solution was aspirated for 10 min. at 0° C. and while being heated

to 90° C., during which time all nitrile was removed.   The solution was then held at 90° C. without aspiration for three-quarters of an hour, after which air was again passed through to remove ammonia formed by hydrolysis of the amide. Experiments with propionamide solutions showed that all the amide was hydrolyzed to ammonia under these conditions.

Results

In Table I are recorded typical unimolecular constants for experiments at various temperatures in which the rate of reaction was measured by determination of both ammonia and amide, and of ammonia alone.   When the data for ammonia production alone are considered, it is evident that at acid concentrations up to and including 4 N there is no indication that rate of ammonia production fails to measure rate of nitrile hydrolysis. At 5 N, however, a small induction period is evident; it becomes very prominent at 6.5 and 8.5 N, although the k values tend to level off in the later stages of the reaction.   With 10 N acid, the induction period again becomes relatively small.

TABLE I

NATURE OF THE INDUCTION PERIOD IN THE HYDROLYSIS OF PROPIONITRILE AT DIFFERENT CONCENTRATIONS OF HYDROCHLORIC ACID

Concentration of hydrochloric acid, normality	Temp., °C.	Analytical method: A—ammonia AA—ammonia + amide	$k \times 10^2$ hr.$^{-1}$ Per cent NH_3*						
			10 – 20	20 – 30	30 – 40	40 – 50	50 – 60	60 – 70	70 – 80
1.00	59.6	A	0.0585 0.0589	0.0582 0.0579					
2.00	59.6	AA	0.152	0.147	0.152	0.154	0.149		
4.00	99.7	A	39.2	40.0		39.7	40.1	39.0	
	99.7	AA	39.7	38.8	39.1	39.8	38.8		
5.02	83.1	A	18.7		20.7	20.4	20.8	20.0 20.4	
	49.6	AA	0.574	0.569	0.584	0.582	0.573	0.586	
6.48	50.1	A	2.00			3.42	3.55	3.56 3.62	
	49.9	AA	3.53	3.51	3.52	3.51	3.48		
8.47	59.6	A	16.9		{23.6 {26.2	32.6	32.7	34.6	32.8
	59.6	AA	122	122	122	117	123	121	
10.13	40.2	A	29.6	30.9		32.0	32.2 31.5	31.8	
	24.7	AA	31.2	30.8	29.1	31.6	29.7	31.4	29.0

* Refers to percentage ammonia for runs analysed for ammonia; given to indicate the region in which k values were determined.

When total amide and ammonia is measured, the induction period is absent at all acid concentrations.   In the concentration range above 4 N, therefore, the rate of amide hydrolysis influences the rate of the over-all reaction and in this range the true rate of nitrile hydrolysis is given by determination of total amide and ammonia, and not of ammonia alone.

The first order velocity constants obtained over a temperature range at each of several acid concentrations are recorded in Table II.   Each value of k is the mean of five or six determinations, total amide and ammonia being measured in every instance.   The average deviation of the observed k values from the recorded mean was usually about 1% for concentrations below 5 N,

TABLE II

UNIMOLECULAR VELOCITY CONSTANTS FOR THE HYDROLYSIS OF PROPIONITRILE WITH
HYDROCHLORIC ACID

Concentration of hydrochloric acid, normality	Concentration of nitrile, normality	Temperature, °C.	$k \times 10^2$ hr.$^{-1}$
0.509*	0.2002	59.6	0.0259
1.00*	0.2002	59.6	0.0584
		83.4	0.762
		93.3	2.03
		99.6	3.92
		111.8	11.1
2.00	0.2002	59.6	0.151
4.00	0.2004	49.6	0.222
		59.6	0.672
		79.7	5.71
		94.0	24.5
		99.7	39.2
4.55	0.2004	59.6	1.18
5.02	0.2239	50.8	0.694
		59.6	1.74
		70.6	5.41
		83.1	20.4
6.48	0.1995	38.3	0.991
		49.9	3.51
		59.6	10.0
		72.6	32.4
8.47	0.1734	30.7	7.19
		38.3	15.6
		59.6	122
10.13	0.1770	0.0	1.67
		16.8	12.1
		24.7	30.4
		34.5	80.2

* At these lower concentrations, a downward drift in velocity due to depletion of the catalyst by ammonia formation was observed and taken into account.

and 1 to 2% for other concentrations. All concentrations were taken without correction as at 25° C., and no correction has been applied for variation of collision number with temperature. These errors partially cancel and should be negligible for comparative purposes.

The constants of the Arrhenius equation, $k = Ae^{-E/RT}$, calculated from the data at each acid concentration, are shown in Table III. The relation was

TABLE III

THE ARRHENIUS CONSTANTS FOR THE HYDROLYSIS OF
PROPIONITRILE AT VARIOUS CONCENTRATIONS
OF HYDROCHLORIC ACID

Concentration of hydro-chloric acid, normality	$\log_{10} A$	E, cal.
1.00	10.04	25,600
4.00	9.95	24,800
5.02	9.68	23,900
6.48	8.92	21,800
8.47	8.85	20,100
10.13	8.78	18,900

satisfactorily obeyed in all cases. To obtain A, the velocity constants were expressed in seconds, and divided by the normality of the solutions to reduce all data to unit acid concentration. Although correct in principle, this procedure is arbitrary as the proper function of acid concentration, in terms of which velocities should be expressed, is not known. This difficulty is common to this and many other investigations of concentrated acid catalysis. Errors in the E values, as determined by consideration of the poorest and best Arrhenius lines, do not exceed 100 to 200 cal. at acid concentrations of 1, 4, and 6.5 N, and 300 to 400 cal. at other concentrations. The probable errors are less than these values.

At hydrochloric acid concentration of approximately 0.5 N, Kilpi (8) has found an activation energy of 25,800 cal. for the hydrolysis of propionitrile

TABLE IV

DATA ILLUSTRATING THE INCREASE OF RATE OF PROPIONITRILE HYDROLYSIS WITH INCREASE
OF HYDROCHLORIC ACID CONCENTRATION (59.6° C.)

Concentration of hydro-chloric acid, normality	0.509	1.00	2.00	4.00	4.55	5.02	6.48	8.47	10.13
$k \times 10^2$ hr.$^{-1}$	0.0259	0.0584	0.151	0.672	1.18	1.74	10.0	122	830*

* *Obtained by extrapolation of the Arrhenius line.*

in alcohol–water medium.   No other data are available with which to make comparison.

Parallelism in changes of A and E, similar to that exhibited in this study, has been frequently observed and has been interpreted by several investigators.

The great sensitivity of the reaction rate to acid concentration is well illustrated in Table IV.   A 20-fold increase in acid concentration results in an increase in rate by a factor of approximately 3×10^4, with no evidence that a maximum rate is attained at higher concentrations, as has been suggested (11).

A few experiments made with sodium chloride present in the reaction solution showed a positive primary neutral salt effect which increased with acid concentration (Table V).   A similar behaviour for hydrocyanic acid has been pointed out before (12).

TABLE V

DATA ILLUSTRATING NEUTRAL SALT EFFECT IN THE
HYDROLYSIS OF PROPIONITRILE BY
HYDROCHLORIC ACID

Hydrochloric acid concentration, normality	Sodium chloride concentration, normality	$k_{49.6°C.} \times 10^2 \text{ hr.}^{-1}$
2.00	—	0.151
	1.9	0.217
4.00	—	0.672
	0.99	0.938

Discussion

The investigation of the system, propionitrile $\xrightarrow{k_1}$ propionamide $\xrightarrow{k_2}$ propionic acid + ammonia, has revealed the interesting fact that it provides an example of consecutive, irreversible unimolecular reactions over the complete range $k_1 \ll k_2$ (below 4 N) to $k_1 \gg k_2$ (estimated above 11 N).   The characteristics of such systems, which constitute the simplest type of successive reactions, have been known for many years, and the existing treatments of the problem in general, and for nitriles and amides in particular (8), are adequate.   A detailed discussion of this aspect of the present study would therefore seem unnecessary.

The nature of the nitrile–amide rate relations derive from the fact that, while the rate of amide hydrolysis increases to a maximum value at hydrochloric acid concentration of about 3 N and then decreases (10), the rate of nitrile hydrolysis increases rapidly and continuously with increase of acid concentration, especially at higher concentrations (Table IV).   The relative rates of the two reactions at 49.6° C., for the concentration range 1.00 to 10.13 N, are recorded in Table VI.   Most of the values have been taken

directly from experimental data or the Arrhenius lines; others were computed as indicated.

TABLE VI

DATA ON THE RELATIVE RATES OF HYDROLYSIS OF PROPIONITRILE AND PROPIONAMIDE

Hydrochloric acid concentration, normality	$k_{49.6°C.} \times 10^2$ hr.$^{-1}$			
	Propionamide (19)	Propionitrile (analysed for NH$_2$ only)	Propionitrile (analysed for total amide +ammonia)	Ratio amide : nitrile*
1.00	39.1	0.0174		2000 : 1
4.00	71.1	0.222	0.219	300 : 1
5.02	54‡	0.573	0.578	90 : 1
6.48	33.9	3.71**	3.42	10 : 1
8.47	15.3	13.2†	47.9	1 : 3
10.13	8.62	8.48	350	1 : 40

* *Given in round figures; the ratio varies with temperature.*

† *Obtained by extrapolation of the k-% reaction curve to 100%.*

‡ *Obtained by interpolation of values at neighbouring concentrations.*

** *This value refers to 50.1° C.*

Adapting Mellor's calculation for consecutive, irreversible, unimolecular reactions (17, p. 118), a slight induction period in the rate of the slowest reaction, as determined by analysis of the final product (in this case ammonia) should be evident when the ratio of the velocity constants is of the order 100 : 1. This corresponds in the present study to acid concentrations of 5 N, where k_2, the amide constant, is the larger, and to 10 N acid, where k_1, the nitrile constant, is the larger, in agreement with the observed behaviour (Table I). The calculations further show that for a ratio of the rate constants of about 10 : 1, a marked induction period should occur, while for smaller values of the ratio the measured velocity of the slowest reaction does not attain its true value. This corresponds to the behaviour found for 6.48 N, where the measured rate eventually equals that of the nitrile, and for 8.47 N where the rate approaches that for the amide (Tables I and VI).

The time curves obtained experimentally at each acid concentration for the amount of nitrile hydrolysed, the amount of ammonia formed, and the concentration of the intermediate amide, each expressed as a percentage of the original concentration of nitrile, are characteristic. In Fig. 1a are shown the curves for 6.48 N acid, characteristic of the type $k_1 < k_2$, while in Fig. 1b are shown those for 8.47 N acid, of the type $k_1 > k_2$. The dotted lines for intermediate amide concentration have been calculated independently from the well known equation,

$$[\text{amide}] = \frac{ak_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right),$$

where a is the initial concentration of nitrile. The values of k_2 obtained in the previous study were used. The agreement between observed results
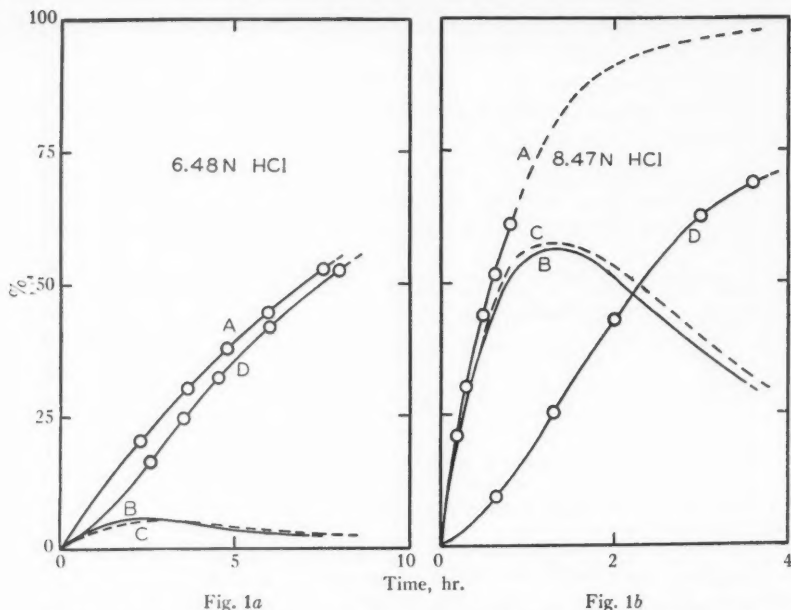
FIG. 1.   *Curves showing the nature of the consecutive reactions of propionitrile and propion-amide at hydrochloric acid concentrations of (a) 6.48 and (b) 8.47 N.   A, nitrile hydro-lysed; B, amide concentration found; C, amide concentration caculated; D, ammonia produced.*

and those calculated on the basis of the analysis of the system presented here is quite satisfactory.

In view of the behaviour revealed by the present study, earlier results (11) obtained for the hydrolysis of propionitrile in concentrated hydrochloric acid solutions contain error since no account was taken of the part played by amide hydrolysis in determining the rate of the over-all reaction.   Actually, the rate measured at 14.9 molal in that investigation corresponds approximately to the rate of amide hydrolysis at this concentration.

An outstanding characteristic of the propionitrile hydrolysis is the rapid increase in rate with acid concentration demonstrated by the data in Table IV. The hydrolysis of other nitriles is analogous to that of propionitrile in this respect.   Krieble and co-workers (11, 12) have related the rapid rate increase to the square of the mean ion activity and, on that basis, have suggested that hydrochloric acid molecules are the principal catalyst.   However, for nitriles other than hydrocyanic acid there is considerable variation in the ratio $k/a_{\pm}^2$ over the range of acid concentrations.   The lack of constancy is apparently not due simply to the fact that their data at higher acid concentrations do not correspond to the rate of nitrile hydrolysis, as neither $k/a_{\pm}$ nor $k/a_{\pm}^2$ have been found to be constant in the present study.   The variation of $a_{\pm}^2$ parallels the large increase within a factor of about twenty over the entire range of

acid concentrations, but other measures of the acid concentration may be adapted to do the same.

The acidity function, H_0, of Hammett (5, p. 267) has been found to be related to the rates of certain acid catalyzed reactions by the expression:

$$H_0 + \log k = \text{constant.}$$

Data for the hydrolysis of cyanamide in nitric acid solutions of concentrations up to 5 N (4) exhibit the theoretical linear relation of unit slope. Using values of H_0 obtained by interpolation or extrapolation of the data of Hammett and Paul (6, 7), the data obtained in the present study have been plotted in Fig. 2. It should be recalled that the values of H_0 given by
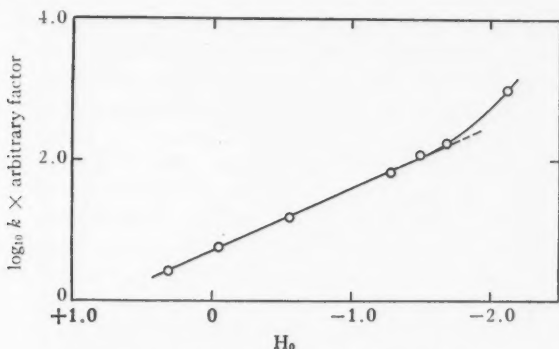
FIG. 2.   *Plot of $\log_{10} k_{59.6°C.}$ against H_0.*

Hammett and Paul refer to indicator solutions in pure acid at temperatures different from those employed here. The graph indicates a linear relation of slope 0.9, for acid concentrations up to 5 N. Deviations from linearity occur at higher concentrations. Reactions which exhibit the relation are, on the basis of the formulation of H_0 by Hammett and the analysis of protic reactions given by Pedersen (18), interpreted as being examples of specific hydrogen ion catalysis. The deviations might indicate general acid catalysis. Alternatively, the reaction may be one of specific hydrogen ion catalysis proceeding through an equilibrium cation, since the assumptions on which the Hammett relation is based may not be valid over the wide range of acid concentration concerned here, where large salt and medium effects may be operative (22). This criterion, therefore, leaves the nature of the catalyst in doubt.

A rapid increase in rate with acid concentration, similar to that observed in the present study, characterizes the cyanamide hydrolysis mentioned previously, and the data have been represented by an empirical relation, formally the same as the familiar one for the primary exponential salt effect. This relation is applicable to propionitrile at concentrations of acid up to 2 to 3 N, but above this concentration the slope increases markedly and con-

tinuously with increase of acid concentration. It may be significant that it is in this region that the activation energy begins to undergo marked change. It would obviously be of interest to know whether the Arrhenius constants change over a range of acid concentrations in the hydrolysis of cyanamide, since such changes may occur where the exponential salt effect is obeyed (9, 14). Schmid and Olsen (20) have studied the neutral salt effect for the cyanamide hydrolysis at salt concentrations as high as 2 to 6 N, at a constant nitric acid concentration of 0.25 N. The study was made at two temperatures only, however, and accurate evaluation of E is not possible from their data. Moreover, the increase of rate with salt concentration is not as marked as that observed for increase of acid concentration.

$\log_{10} k/N$ (59.6° C.) $\times$ arbitrary factor
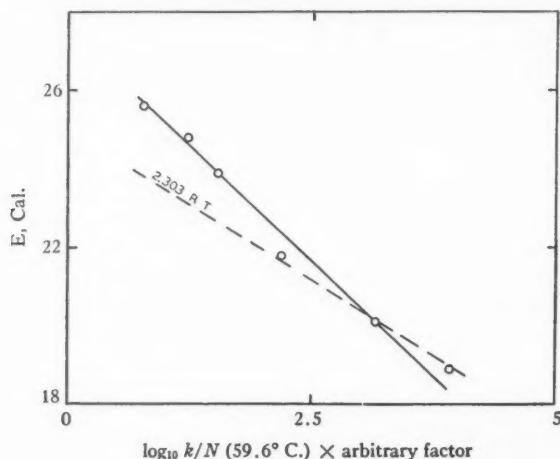
FIG. 3.   *Plot of $\log_{10} k_{59.6°C.}$ against E.*

Actually, the rapid rate increase with acid concentration shown in Table IV can be accounted for by the observed decrease in activation energy. In Fig. 3 are plotted the values for log k/N against the corresponding activation energies for different acid concentrations. Simultaneous, parallel variation of the A factor may be assumed responsible for deviations from a linear relation of theoretical slope, 2.303 RT, and cause an increase in slope. Its magnitude, however, is of the proper order. At concentrations of 6.48, 8.47, and 10.13 N, where small variation in A occurs, the points lie about a line of theoretical slope.

It seems probable that the observed decrease in activation energy with increased acid concentration represents a fundamental variation. A possible explanation of the decrease, based on the assumption of two catalytic species whose concentrations vary with acid concentration, e.g., oxonium ion and undissociated acid molecules, of which the latter is characterized by a lower activation energy, seems untenable. If this were true, not only would the

difference in activation energies have to exceed 6.7 Cal. but there would be sufficient of the more efficient catalyst at all acid concentrations for the reaction to proceed exclusively through its agency.

Another possibility, namely, that a temperature dependence of E may cause an apparent variation over the acid concentration range because of the different temperature ranges employed for different acid concentrations, appears to be excluded. The magnitude of the observed shift, the generally small temperature dependence of E above 40° C. (14, 15, 16), and the fact that variation in E occurs between acid concentrations studied over the same temperature ranges (1 and 4 N; 6.5 and 8.5 N), are all opposed to such a likelihood.

Dependence of the Arrhenius constants on temperature and variation of this dependence with acid concentration might result in apparent shifts in E and A (2). Hydrolytic reactions are of the type which display temperature dependence of activation energy (13). Furthermore, in calculating the activation energies, it was not possible to take account of the variation in dielectric constant of the medium with temperature. Reactions of zero ionic type, to which class the hydrolysis of propionitrile belongs, are least sensitive to variations in the dielectric constant (1, 21), although at the high acid concentrations employed here the effect may be uncertain. Also, temperature dependence is usually of decreasing importance in the temperature regions used in the present work, with exception of the experiments at an acid concentration of 10 N. No evidence for its existence can be observed from the Arrhenius lines, even in the experiments with 1 and 4 N acid, where the most accurate measurements were made and where five temperatures were used over a range of 50° C. It is possible, of course, that the best accuracy attained in the study might be inadequate to detect failure of the Arrhenius equation. Since the temperature variations of A and E partially compensate, the total possible effect in this eventuality might be expected to be small. Hence, it is believed that, while small temperature dependence of A and E may possibly have some effect here, the variations of A and E with concentration are substantially real.

For reactions in which real changes in A and E occur with variation of catalyst concentration, apparent relations between reaction rate and other factors such as mean ion activity, acidity function, salt effect, etc., probably do not represent fundamental analysis of the factors influencing the reaction.

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THE SYNTHESIS AND THE CHARACTERIZATION OF THE MONOMETHYL- AND THE DIMETHYL-QUINOLINES[1]

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Abstract

All 7 monomethyl- and all 21 dimethyl-quinolines were synthesized by unambiguous methods and those solid above room temperature were purified to their maximum melting points. The picrates, styphnates, and trinitro-*m*-cresolates of each quinoline were prepared and their properties recorded. The picrates in particular were purified to their ultimate melting points. Incidentally, 7-ethyl-quinoline and a number of trimethyl-quinolines were also prepared. It is concluded that the melting points previously given in the literature for most of the picrates are of little use for identification purposes.

Introduction

The preparation of all the monomethyl-quinolines and many of the dimethyl-quinolines has already been recorded. They were prepared by a variety of methods and by many different investigators, and it is not unusual that the recorded properties for the same substance vary by more than reasonable experimental errors. In the course of some degradation experiments with alkaloids, two of the present authors (R.H.F.M. and L.M.) obtained lepidine and 7-methyl-quinoline and found that the melting points of their purified picrates were considerably higher than any values thus far recorded for these well known compounds. Concurrently a dimethyl-quinoline was obtained from the degradation products of another alkaloid. The melting point of its picrate was sufficiently close to the melting points of a number of picrates already described to justify their preparation for purposes of authentication. Here again the recorded values were found to be in serious error, and it was concluded that the literature values for the melting points of the picrates of most of the monomethyl- and dimethyl-quinolines were of little service in identifying such substances. As subsequent events have proved, this conclusion was amply justified.

The 7 monomethyl-quinolines and the 21 dimethyl-quinolines have been prepared by unambiguous syntheses. The 10 quinolines that were solids at room temperature were purified to their maximum melting points, and the picrates, the styphnates, and the trinitro-*m*-cresolates were prepared from all bases after exhaustive purification. The accompanying table is a summary of the melting points of these derivatives. In general the picrates attained their ultimate melting points without further purification, but as a precaution they were all recrystallized at least once. Only when the synthesis produced two substances was it necessary to repeat the recrystallization. The styphnates and the trinitro-*m*-cresolates were not recrystallized except when the

quinoline was known to contain isomers.   Their melting points are therefore not quite as accurate as those of the picrates, but they are sufficiently so to be serviceable for purposes of identification.   Further purification would in fact serve little purpose since the styphnates melt with rather vigorous decomposition, and the highly purified trinitro-*m*-cresolates do not melt quite as sharply as do the picrates.   On the other hand, even when the melting points of the picrates are very high there is never more than a one-degree difference between incipient shrinking and complete fluidity.   It is the latter figure that is here recorded.   An inspection of the table reveals the fact that any monomethyl- or dimethyl-quinoline can be positively identified by the preparation of its three derivatives.

It has been found that the purity of the reagents used in making the derivatives is of paramount importance.   Picrates made from reagent grades of commercial picric acid melted either at a slightly lower temperature or not quite sharply, and repeated recrystallization did not serve to achieve much purification.   It is conceivable that picric acid as ordinarily prepared contains a small amount of styphnic acid.   The latter is more soluble in water and recrystallization of the purest commercial grades from this solvent yielded a satisfactory product (m.p. 122.6° C.)*.   For the preparation of the other derivatives the styphnic acid and the trinitro-*m*-cresol were the purest commercial specimens recrystallized from hot water; they then melted at 178° C. and 109° C. respectively.

The elementary micro-analysis of the picrates for nitrogen and for carbon and hydrogen offers no difficulties.   The styphnates decompose with considerable vigour and good carbon and hydrogen analyses were not obtainable, but analyses for nitrogen were not specially difficult.   The trinitro-*m*-cresolates behaved like the styphnates.

The choice of derivatives alternative to the picrates was not an easy one. The flavianates are sparingly soluble well crystallized compounds, but their melting points are indefinite and too high to be useful.   The picrolonates are not easily prepared and most of them are too soluble.   Crystalline derivatives of 2 : 4-dinitro-phenol could not be obtained out of alcohol, and the chromates do not appear to be entirely satisfactory for analysis nor for recrystallization.

It seems advisable to point out that quinolines isolated from mixtures do not readily yield picrates of the correct melting points.   When the melting point cannot be appreciably raised by further recrystallization it is advisable to regenerate the quinoline, distil, and reject end fractions.   The picrate may then be recrystallized alternately from acetone–methanol, from water, and again from acetone–methanol.   In most cases the solubility in boiling methanol is too low for convenient recrystallization except when the quantity is very small.   There have been many occasions to determine the melting points of known mixtures of picrates and other derivatives.   It was invariably found that the melting point depression was sufficient to be easily recognized.   For

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* All melting points are corrected.

example, a mixture of the picrates of 4 : 5- and of 4 : 8-dimethyl-quinoline is completely liquid at 205 to 210° C. and a mixture of the trinitro-*m*-cresolates of 2- and of 3-methyl-quinoline melted completely at 203° C.

TABLE I

MELTING POINTS OF MONOMETHYL- AND DIMETHYL-QUINOLINE DERIVATIVES

Quinolines and their melting points			Picrate, m.p., °C.	Styphnate, m.p., °C.	Trinitro-*m*-cresolate, m.p., °C.
2-Methyl			195	219	223
3-			190	190	223
4-			220	237	254
5-			223	218	214
6-			235	234	238
7-			242	242	243
8-			205	202	199
2 : 3-Dimethyl,		70°	235	243	248
2 : 4-			196	212	211
2 : 5-	††		223	207	201
2 : 6-		60°	191	200	206
2 : 7-	†	61°	196	222	250
2 : 8-			183	194	209
3 : 4-		74°	221	232	237
3 : 5-	††		220	214	221
3 : 6-	††	58°	253	234	255
3 : 7-	††	80°	244	214	222
3 : 8-			210	205	208
4 : 5-	††	78°	233	227	230
4 : 6-			249	221	244
4 : 7-			230	272*	228
4 : 8-		58°	229	231	231
5 : 6-	††	50°	201	205	202
5 : 7-	††		249	247	239
5 : 8-			186	184	180
6 : 7-	†	58°	278	259*	262*
6 : 8-			230	190	184
7 : 8-	††		198	179	214

† *Quinolines previously prepared but picrate not made.*
†† *Quinolines not previously known.*
* *With gradual decomposition.*

The Syntheses

There is no question but that the Skraup synthesis with its modifications has proved the most widely applicable of all syntheses for the preparation of quinolines. It was used wherever possible. Some of the necessary amines were not readily obtainable and occasionally the corresponding nitro compounds were even less available. Picric acid was used as the oxidizing agent in a number of preparations, but recently it was observed that *o*-nitrophenol offers a number of advantages. Its slight but appreciable volatility tends to dissipate some heat during the original exothermal reaction and any hydroxy-quinoline formed from the amino-phenol would not distil from the alkaline solution. By using the Cohn boric acid method (5) and *o*-nitrophenol as the oxidizing agent, a yield of 91.8% was obtained in one preparation.

There has been some confusion in regard to the position of ring closure of
m-substituted anilines where two products can be obtained (7, 24).   *m*-Tolui-
dine can give rise to both 5- and 7-methyl-quinolines and both appear to be
produced.   However, by far the greater proportion of the base consists of the
7-methyl compound.   The 5-methyl derivative was prepared by an unam-
biguous route from 4-nitro-3-amino-toluene and the nitro group in the resulting
8-nitro-5-methyl-quinoline eliminated   by   reduction   and   diazotization.
Similarly, 4-*o*-xylidine yielded a mixture of 5 : 6- and 6 : 7-dimethyl-quinolines
(2), but the 6 : 7-isomer was readily obtained in a pure condition by direct
crystallization, and the 5 : 6-isomer was obtained in a pure form from the
mother liquor as its picrate.   The latter was also synthesized via its 8-nitro
derivative from 4-amino-5-nitro-*o*-xylene.   All the other mono- and dimethyl-
quinolines substituted only in the benzene nucleus were obtained without
ambiguity from the appropriate amines.

The 2-methyl-quinolines containing no other substituent in the pyridine
nucleus were prepared by the Doebner and v. Miller synthesis (8). The only
ambiguity here is the quinoline derived from *m*-toluidine to which Decker and
Remfry (7) assigned the 2 : 5-formula.   That this assumption was unwarranted
was shown by the preparation of 2 : 5-dimethyl-quinoline via the 8-nitro
compound from 4-nitro-3-amino-toluene, and proving that it was not identical
with that obtained directly from *m*-toluidine which must therefore be the
2 : 7-dimethyl-quinoline.   An attempt to isolate the 2 : 5-isomer from the
mother liquors of the latter synthesis was only partly successful.   The picrate
was ultimately obtained but it was not pure, and this is attributed to the fact
that the *m*-toluidine contained small amounts of the *o*- and *p*-isomers.   The
3-methyl-quinolines, exclusive of the 2 : 3-dimethyl compound, were prepared
by an adaptation of the Skraup conditions to the appropriate amine and a
substituted acrolein.   The Shell Development Co., Emeryville, Cal., kindly
provided a generous supply of α-methylacrolein from which it was possible
to synthesize the necessary bases in reasonable yields.   The nitro compounds
corresponding to the amines and *o*-nitrophenol were used as oxidizing agents.
As in other similar ring closures *m*-toluidine yielded the 7-substituted com-
pound, namely, 3 : 7-dimethyl-quinoline, but it was possible to isolate an
appreciable amount of 3 : 5-dimethyl-quinoline from the liquid fraction of the
base.   The 3 : 5-isomer was unambiguously synthesized via its 8-nitro
derivative.

The synthesis of 3 : 4-dimethyl-quinoline was readily achieved by con-
densing aniline with 2-methyl-3-keto-*n*-butanol under the above conditions
(2, 4).   It proved to be identical with a specimen of 3 : 4-dimethyl-quinoline
obtained in unsatisfactory yield by condensing *o*-amino-acetophenone with
propionaldehyde (10).

The yields of the 3 : 4-dimethyl-quinolines were so good by the modified
Skraup reaction that at one time an attempt was made to prepare the 3-
substituted quinolines by eliminating the 4-methyl group.   The condensation
of 3 : 4-dimethyl-quinoline with chloral proceeded readily but hydrolysis of

the condensation product with alkali yielded only a small amount of the 4-acrylic acid, most of the condensation product under our conditions regenerating the dimethyl-quinoline. Examples of alkaline hydrolysis effecting the rupture of a double bond are rare. An analogous case is recorded by Perkin and Robinson (20) who observed that boiling α-cyano-2 : 3-dimethoxy-cinnamic acid with alkali yielded 2 : 3-dimethoxy-benzaldehyde. Furthermore, oxidation of the 4-acrylic acid to the 4-carboxylic acid and decarboxylation of the latter yielded only a small amount of impure 3-methyl-quinoline.

The 4-methyl-quinolines were prepared by applying the procedure of Mikhailov (16) for the preparation of lepidine by substituting the toluidines for aniline. The 4 : 6- and 4 : 8-dimethyl compounds were obtainable without ambiguity from *p*- and *o*-toluidine respectively. The base obtained from *m*-toluidine may have contained a small amount of 4 : 5-dimethyl-quinoline, although no difficulty was encountered in obtaining the picrate of 4 : 7-dimethyl-quinoline in a pure condition.

It was shown in a preliminary experiment that pure quinoline can be isolated from the products obtained by passing 8-methoxy-quinoline over heated zinc dust in an inert atmosphere. An attempt to prepare 4 : 5-dimethyl-quinoline from its 2-hydroxy-8-methoxy derivative by the same procedure ultimately yielded a satisfactory product, but the yield was so small that it was also prepared in another way. It appears that a small amount of elimination or wandering of methyl groups occurs under these conditions, and it is not unlikely that the zinc-dust distillation of the carbostyrils suffers from the same objection. The picrates melted at a temperature appreciably higher than Ewins and King (9) have recorded for the same compounds prepared by the same method, even when allowance was made for temperature corrections. Ewins and King purified their pyrolytic products via the picrates but it now appears that their procedure was inadequate to eliminate compounds that might have been formed by the loss or wandering of a methyl group.

It was eventually demonstrated that the desired 4 : 5-dimethyl-quinoline could be prepared from 4-nitro-3-amino-toluene. This was condensed with 3-keto-*n*-butan-1-ol under the Doebner and v. Miller conditions to give a small amount of 8-nitro-4 : 5-dimethyl-quinoline. Elimination of the nitro group via the amino group gave a very small yield of the required base, which was obtained crystalline and purified as such.

At this point the possibility of removing a bromine atom from the benzene nucleus by the procedure of Girardet (11) was investigated, having in mind that it might be used to block one of the positions ortho to the amino group. For this purpose 3-methyl-6-bromo-quinoline was prepared. Reduction with the zinc-copper couple eliminated the halogen but at the same time partly reduced the quinoline. It was necessary to dehydrogenate the latter to yield 3-methyl-quinoline, which was then relatively pure.

The 2 : 3-dimethyl-quinoline was prepared by condensing isatoic acid with methyl-ethyl ketone and decarboxylating the resulting 2 : 3-dimethyl-

quinoline-4-carboxylic acid.   The synthesis of 2 : 4-dimethyl-quinoline from o-amino-acetophenone and acetone proved to be impracticable both on account of the poor yield and the difficulty of obtaining a pure substance. The Skraup reaction when applied to aniline and 4-keto-pentan-2-ol yielded the desired substance in a satisfactory state of purity (13).

Incidentally, 7-ethyl-quinoline and a number of trimethyl-quinolines have been prepared and are described in the experimental section.

All crystalline new compounds here described were analysed for at least one element.   Where the properties of previously known substances varied by more than a reasonable amount from recorded values they were also analyzed.   It remains to be added that all the melting points were determined in a sulphuric acid bath with Anschütz thermometers and are therefore practically corrected. The apparatus has repeatedly been checked with compounds of known melting points.   After an approximate value had been determined, the value was more accurately determined, the rate of heating being decreased as the melting point was reached.   The fresh sample was placed in the bath at a temperature about 20° C. below its melting point.   All recorded melting points have been checked a number of times and one of the writers (R.H.F.M.) has determined the melting points of all picrates on at least two occasions.

It is deemed impracticable to give all the references relevant to the many published researches upon which this work is based.   Such a list would add greatly to the length of the present paper.   It also seemed unnecessary to cite the many values for the melting points of the bases and the picrates as recorded by previous investigators.

Experimental

As progress from one preparation to the next was made, a great deal was learnt about the many reactions that were used.   It is therefore obvious that the yields were not always the maximum attainable.   For this reason it is deemed expedient to select only a few typical experiments for detailed description.   In these the yields are probably the best that can be achieved unless some new procedure is discovered.

When the quinoline itself was a solid at room temperature it was recrystallized from specially purified hexane until there was no further increase in melting point.

The picrates were prepared by adding a hot methanolic solution of the quinoline to a solution of excess picric acid in hot methanol.   In general, the picrate was filtered off while the mixture was still warm, and washed with methanol.   The picrate was then recrystallized either from boiling methanol or from a mixture of acetone and methanol.   With the single exception of 7-methyl-quinoline picrate there was no appreciable increase in the melting points of the picrates on recrystallization.   The styphnates and trinitro-m-cresolates were prepared exactly as the picrates, but only the 7-methyl-quinoline derivatives were recrystallized.

The Skraup Syntheses

The following synthesis is one employing the Cohn boric acid method (5) but instead of using the nitro compound corresponding to the amine, *o*-nitrophenol was used as the oxidizing agent. Its use in this connection appears to be new. It possesses distinct advantages over picric acid, which was also used in a number of syntheses. Its ready solubility in the sulphuric acid brings it into intimate contact with the reactants, and, owing to its volatility, it acts as a heat sink, and when the reaction is completed the excess can easily be removed by steam distillation.

7-Ethyl-quinoline

To a mixture of 3.5 gm. of ferrous sulphate, 12 gm. of *m*-ethyl-aniline, 8.3 gm. of *o*-nitrophenol, and 6.5 gm. of boric acid dissolved in 37.5 gm. of glycerol was added slowly and with shaking 18 cc. of concentrated sulphuric acid. The mixture was gradually heated to boiling and then boiled under reflux for three hours. At no time was there any evidence of a violent reaction.

The somewhat diluted mixture was distilled in a current of steam to remove the excess nitrophenol, made alkaline, and the quinoline was then distilled in steam. The base obtained from the distillate was purified in the usual manner by diazotization, etc. There was obtained 14.6 gm. of 7-ethyl-quinoline presumably contaminated with a small amount of 5-ethyl-quinoline. This corresponds to a yield of 91.8% based upon the *m*-ethyl-aniline, and the writers believe that it is the highest ever recorded for a Skraup synthesis.

The picrate was recrystallized twice from acetone-methanol; m.p. 229° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.71%. The styphnate melted at 268° C. and the trinitro-*m*-cresolate at 240° C.

8-Nitro-5-methyl-quinoline

A mixture of 25 gm. of ferrous sulphate, 15 gm. of 4-nitro-3-acetylamino-toluene, 3 gm. of picric acid, 26 cc. of glycerol, 4 gm. of boric acid, and 11 cc. of sulphuric acid was boiled for 3.5 hr. The 8-nitro-5-methyl-quinoline was isolated as in the case of the corresponding 5 : 6-dimethyl-quinoline derivative (*vide infra*) and recrystallized three times from hot ethanol.

There was obtained 3.2 gm. of the compound, which melted at 138° C. Calc. for $C_{10}H_8O_2N_2$: N, 14.89%. Found: N, 14.95%.

The 3-amino-4-nitro-toluene required in this and later syntheses was prepared from *m*-cresol (25) through the following stages,—3-hydroxy-4-nitro-toluene (m.p. 56° C.), 3-ethoxy-4-nitro-toluene (m.p. 52° C.), and 3-amino-4-nitro-toluene (m.p. 112° C.). The last stage was carried out in an autoclave with aqueous ammonia and a little ethanol (12). The yield was 59%.

5-Methyl-quinoline

The reduction of 8-nitro-5-methyl-quinoline (3.17 gm.) with iron and hydrochloric acid yielded the sparingly soluble hydrochloride of 8-amino-5-methyl-quinoline in dark red prisms, which began to char at 200° C. The free base (1.65 gm.) was obtained as a pale yellow oil, b.p. 115° (1.5 mm.).

The picrate was obtained in brilliant red needles melting at 234° C.   Calc. for $C_{16}H_{13}O_7N_5$: C, 49.62; H, 3.36; N, 18.09%.   Found: C, 49.99; H, 3.72; N, 18.29%.

The amino-quinoline (1.63 gm.) was diazotized in hydrochloric acid and then treated with hypophosphorous acid (15).   The basified solution was distilled in a current of steam and the quinoline distilled twice *in vacuo*, b.p. 85° (1 mm.); yield, 1.03 gm.   It was obtained as an almost colourless oil, which yielded a picrate moderately soluble in boiling methanol.   Calc. for $C_{16}H_{12}O_7N_4$: N, 15.05%.   Found: N, 15.00%.

6-Methyl-, 7-Methyl-, and 8-Methyl-quinoline

These three methyl-quinolines were prepared by the Clarke and Davis (4) procedure from the requisite toluidines, which had been previously distilled. The quinolines were repeatedly distilled *in vacuo*.   The 6- and 8-methyl-quinolines yielded pure picrates without further recrystallization.   The picrate of 7-methyl-quinoline as prepared in methanol melted at 235° C.   When recrystallized twice more from acetone-methanol it melted at 242° C. and further recrystallization did not alter this value.   Calc. for $C_{16}H_{12}O_7N_4$: N, 15.05%.   Found: N, 15.10%.

The styphnate of 7-methyl-quinoline was recrystallized twice from acetone-methanol.   It consisted of fine colourless prisms melting with vigorous decomposition at 242° C.   Calc. $C_{16}H_{12}O_8N_4$: N, 14.43%.   Found: N, 14.45%.

The trinitro-*m*-cresolate was obtained in fine yellow prisms with a greenish cast.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.55%.

5 : 7-Dimethyl-quinoline

This quinoline was prepared by the procedure of Clarke and Davis (4). There was used 14.4 gm. of ferrous sulphate, 38 gm. of 5-nitro-1 : 3-dimethyl-benzene, 50 gm. of 5-amino-1 : 3-dimethyl-benzene, 123 cc. of glycerol, and 72 cc. of sulphuric acid.   Gentle heating brought about an exothermal reaction that kept the mixture boiling for 15 min., after which it was boiled for four hours.

The quinoline was isolated in the usual way; it weighed 4.8 gm.   On cooling, the base yielded a colourless mass of crystals that melted at 22° C.   For the preparation of its picrate it was redistilled twice, large end fractions being rejected.   Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.63; N, 14.51%.   Found: C, 52.79; H, 3.73; N, 14.58%.

5 : 8-Dimethyl-quinoline

The 2-amino-*p*-xylene required for the 5 : 8-compound was isolated from commercial xylidine as hydrochloride, and this was recrystallized several times from dilute hydrochloric acid (18).   The quinoline (Skraup) was obtained as an almost colourless oil, which on cooling formed a colourless solid that remelted at 2° C.   The picrate was analysed.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.46%.

6 : 7-Dimethyl-quinoline

The 4-amino-*o*-xylene required for the preparation of the 6 : 7-base was prepared from crystalline 4-nitro-*o*-xylene (6), purified as its acetyl derivative, and used as such. The yield of redistilled quinoline (Skraup) was 67% of the theoretical. It solidified on cooling, leaving a small amount of oil that was removed by prolonged draining at the pump (2). The solid was recrystallized twice from purified hexane; it then melted at 58° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 9.14%. The colourless stout prisms possess an odour suggestive of camphor as well as of quinoline. The picrate was prepared from the recrystallized base. It was virtually insoluble in hot methanol and only very sparingly soluble in boiling acetone, from which solvent a small amount was recrystallized with unaltered melting point. Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85, H, 3.63%. Found: C, 53.05; H, 3.97%.

The oil from which the 6 : 7-dimethyl-quinoline had been filtered was dissolved in a large volume of hot methanol, and the solution treated with a hot methanolic solution of picric acid in slight excess. The solid that separated consisted largely of the picrate of the 6 : 7-base. It was filtered hot and the picrate, which crystallized from the cooled filtrate, was recrystallized from acetone–methanol until the melting point was sharp and constant at 201° C. The picrate was then completely soluble in either hot methanol or hot acetone and when admixed with a specimen of 5 : 6-dimethyl-quinoline picrate prepared as described below it melted at 201° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.59%.

The free base was regenerated from the picrate by shaking the latter with ammonia in the presence of ether. The solvent was removed from the washed extract and the residue distilled. On cooling, it solidified at once and when recrystallized from hexane it melted sharply at 50° C. The picrate prepared from the crystalline base also melted at 201° C. There was isolated about 1.4 gm. of this base from 20 gm. of the mixture.

8-Nitro-5 : 6-dimethyl-quinoline

A mixture of 9.7 gm. of ferrous sulphate, 60 gm. of 5-nitro-4-acetylamino-1 : 2-dimethylbenzene (19), 12 gm. of picric acid, and a solution of 17 gm. of boric acid in 82 gm. of glycerol, was treated with 44 cc. of sulphuric acid, and boiled under reflux for 3.5 hr.

The cooled and diluted solution was filtered to remove some resin and then basified with caustic soda. The filtered and washed precipitate was extracted with a hot 1 : 1 alcohol-benzene mixture. The solvent was removed from the extract and the solid residue distilled *in vacuo*. There was obtained 10 gm. of a pale yellow solid, which, when recrystallized from hot methanol, melted sharply at 166°. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%. Found: N, 13.76%.

When the nitro-quinoline was reduced with stannous chloride in the presence of hydrochloric acid, a sparingly soluble stannichloride was formed. This was decomposed only slowly in the presence of sodium hydroxide. The recovered base was extracted with benzene, distilled *in vacuo*, and recrystal-

lized from methanol; m.p. 78 to 79° C.   The mono-picrate crystallized from methanol in orange coloured needles melting at 213° C.   Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%.   Found: N, 17.28%.

5 : 6-Dimethyl-quinoline

When this quinoline was prepared from its 8-amino derivative the authors were not acquainted with the hypophosphorous acid reduction of diazonium compounds (cf. preparation of 5-methyl quinoline).   A solution of 2 gm. of 8-amino-5 : 6-dimethyl-quinoline in 20 cc. of ethanol and 0.5 cc. of sulphuric acid was diazotized in the cold with a saturated aqueous solution of sodium nitrite and then heated on the steam-bath to complete the reaction and to remove the acetaldehyde and most of the alcohol.   The solution was then treated with sodium hydroxide and distilled in a current of steam.   The distillate was extracted with benzene and the residue from this solvent distilled *in vacuo*.   There was obtained a low boiling fraction (about 90° (3 mm.)), which was converted into its picrate.   This, when recrystallized from methanol, melted sharply at 201° C. either alone or in admixture with the above described picrate of 5 : 6-dimethyl-quinoline.

The higher boiling fraction was also converted into its picrate and this recrystallized from methanol; m.p. 224° C.   Analysis indicates that it is the picrate of 8-ethoxy-5 : 6-dimethyl-quinoline.   Calc. for $C_{19}H_{18}O_8N_4$:   N, 13.02%.   Found: N, 13.60%.

6 : 8-Dimethyl-quinoline

This base was obtained in 70% yield (Skraup) from 4-*m*-xylidine, which was purified via its acetate (18).   The quinoline was redistilled a number of times, liberal end fractions being discarded.

7 : 8-Dimethyl-quinoline

The procedure of Clarke and Davis gave a 50% yield.   The 3-amino-*o*-xylene was prepared from a specimen of 3-nitro-*o*-xylene that had been exhaustively fractionated to eliminate the 4-nitro isomer.   The quinoline was redistilled three times, each time without actual boiling of the liquid.   The picrate was analysed.   Calc. for $C_{17}H_{14}O_7N_4$:   N, 14.51%.   Found: N, 14.52%.

2-Methyl-quinoline (Quinaldine)

Quinaldine and the other 2-methyl-quinolines (except the 2 : 3- and the 2 : 4-compounds) were prepared by the Doebner and v. Miller synthesis as modified by Mills, Harris, and Lambourne (17).   The quinaldine itself was redistilled a number of times and the fraction boiling at 110° (6 mm.) collected separately.

2 : 5-Dimethyl-quinoline

The substitution of 3-amino-4-nitro-toluene (12) for aniline in the procedure of Mills, Harris, and Lambourne (17) for the synthesis of quinaldine yielded 8-nitro-2 : 5-dimethyl-quinoline.   The cooled and diluted reaction mixture was filtered to remove the resins, basified with sodium hydroxide, and the

solid nitro base filtered, washed with water, dried, and sublimed *in vacuo* (140 to 160° (1.5 mm.)).   It was recrystallized from boiling methanol from which it separated as long, stout, white needles melting at 174° C.   Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%.   Found: N, 13.82%.

8-Nitro-2 : 5-dimethyl-quinoline (3 gm.) when reduced with iron and alcoholic hydrochloric acid yielded 8-amino-2 : 5-dimethyl-quinoline as a yellowish oil, b.p. 110 to 115° (1.5 mm.), weighing 1.93 gm.   A small quantity was converted to the picrate, which, after recrystallization from methanol, consisted of small bright red prisms, m.p. 189°.   Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%.   Found: N, 17.49%.

Treatment of diazotized 8-amino-2 : 5-dimethyl-quinoline (1.90 gm.) with hypophosphorous acid according to Mai's procedure (14) yielded 2 : 5-dimethyl-quinoline as an oil, b.p. 80 to 85° (1 mm.) (1.01 gm.).   The picrate was obtained from methanol in slender, soft, yellow needles.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.32, 14.35%.

2 : 6-Dimethyl-quinoline

This substance was prepared by the method of Mills, Harris, and Lambourne (17), in which *p*-toluidine (175 gm.) was substituted for aniline.   There was obtained 75 gm. of distilled oil, b.p. 104° C. (1 mm.), which crystallized on cooling.   The crystalline 2 : 6-dimethyl-quinoline was separated from a small quantity of oil by filtration through a fritted glass funnel.   After two recrystallizations from petroleum ether it was obtained as small, stout prisms, melting at 60°.   The picrate formed in methanol is dimorphous.   It separated first in small crystals that melted indefinitely between 187 and 191°, but on standing in the presence of methanol the crystals changed to a larger form melting sharply at 191°.   The higher melting form is obtained when either form is recrystallized from hot acetone-methanol

2 : 7-Dimethyl-quinoline

This base was prepared from *m*-toluidine, paraldehyde, and concentrated hydrochloric acid, as described by Doebner and v. Miller (8).   The product consisted of an oil, b.p. 115 to 116° C. (7 mm.), which largely solidified on cooling in the refrigerator.   The crystals were separated from the adhering oil by filtration on a fritted glass funnel and then recrystallized from petroleum ether, m.p. 61°.

The filtered oil was converted to the picrate.   From the more soluble fraction an impure picrate melting indefinitely at 205 to 210° C. was obtained.   This was achieved by alternately recrystallizing the more soluble fractions from methanol and from water.

2 : 8-Dimethyl-quinoline

This quinoline was obtained by the method of Mills, Harris, and Lambourne (17), using *o*-toluidine instead of aniline.   It consists of a straw-coloured oil, b.p. 93 to 95° (2 mm.).   The trinitro-*m*-cresolate was obtained in yellow rectangular plates, which on exposure to light assumed a grey colour.   This colour change did not affect the melting point.

2 : 3-Dimethyl-quinoline

This was prepared from isatin and methyl-ethyl-ketone by the method of Pfitzinger (21) as modified by Plant and Rosser (22). It is a solid that crystallizes from petroleum ether, m.p. 70.5°. The picrate separates from methanol in short, stout, yellow prisms. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.50%.

2 : 3 : 6-Trimethyl-quinoline

The starting material for this synthesis was 5-methyl-isatin, m.p. 187° C., prepared in 88.2% yield from *p*-toluidine by the method of Sandmeyer as described in "Organic Syntheses" (15). The 5-methyl-isatin was condensed with methyl-ethyl-ketone as in the preparation of 2 : 3-dimethyl-quinoline. The 2 : 3 : 6-trimethyl-quinoline-4-carboxylic acid (38% yield) was dried and decarboxylated by distillation. 2 : 3 : 6-Trimethyl-quinoline distilled as a heavy oil that crystallized immediately. After two recrystallizations from petroleum ether it had a constant melting point of 87.5°. The picrate, prepared in methanol, separated as lemon-yellow leaflets, m.p. 217°. The styphnate and the trinitro-*m*-cresolate melted at 238° and at 224° respectively.

2 : 3 : 8-Trimethyl-quinoline

This was prepared from 7-methyl-isatin (m.p. 275° C., obtained from *o*-toluidine in 23.4% yield) by condensation with methyl-ethyl-ketone. The 2 : 3 : 8-trimethyl-quinoline-4-carboxylic acid (23% yield) thus produced was decarboxylated by distillation at atmospheric pressure. 2 : 3 : 8-Trimethyl-quinoline was obtained as a heavy oil that crystallized immediately, b.p. 85 to 95° (1 mm.). After two recrystallizations from petroleum ether it separated as colourless prisms melting at 56 to 57°. The picrate crystallized from methanol as light yellow needles melting at 252°. The styphnate and the trinitro-*m*-cresolate melted at 239° and at 227° respectively.

2 : 4-Dimethyl-quinoline

To a mixture of 10 gm. of ferrous sulphate, 25 gm. of aniline, 17 gm. of nitrobenzene, and 30 cc. of sulphuric acid, which was maintained at 160° C., was added dropwise 25 gm. of 4-keto-pentan-2-ol (prepared by condensing acetone with acetaldehyde (3)). After heating under gentle reflux for 6.5 hr. the quinoline was isolated from the reaction products as in the Skraup procedure. There was obtained 8 gm. of a colourless product of constant boiling point.

The picrate prepared from a middle fraction was moderately soluble in hot methanol, from which it was obtained in brilliant yellow plates.

The yield of 2 : 4-dimethyl-quinoline by condensing acetone with *o*-amino-acetophenone was very poor (10). Nevertheless, there was obtained a sufficient quantity of the base to permit adequate purification of it and recrystallization of the picrate to constant melting point (196° C.).

3-Methyl-quinoline

Method I. A gently boiling mixture of ferrous sulphate (4 gm.), aniline (8 gm.), nitrobenzene (7.0 gm.), and sulphuric acid (15 cc.) was slowly heated

with α-methylacrolein dimethyl-acetal (10 gm.) (27) and heating continued for several hours.   The quinoline was isolated in the usual way and converted to the picrate, which, when twice recrystallized, melted at 188° C.

Method II.   The procedure used was that employed in the preparation of 3 : 7-dimethyl-quinoline.   From 15 gm. of ferrous sulphate, 33 gm. of aniline, 20 gm. of *o*-nitrophenol, 44 cc. of sulphuric acid, and 32 gm. of α-methyl-acrolein, there was obtained 20 gm. of once distilled 3-methyl-quinoline. For the preparation of the picrate and other derivatives the base was redistilled twice, the last time 1 gm. being collected from the middle fraction.   The picrate melted at once at 190° C. and recrystallization did not raise this value.

3 : 4-Dimethyl-quinoline

Method I. (Camps' synthesis).   A mixture of 5 gm. of *o*-amino-acetophenone and 3 gm. of propionaldehyde was heated to 225° C. for one hour in a sealed tube.   The acidified product (dilute sulphuric acid) was distilled in a current of steam, cooled, diazotized, distilled in steam, basified with sodium hydroxide, and again distilled in steam.   The distillate yielded to benzene extraction a small amount of oil, which, when distilled, weighed 0.5 gm.   The picrate was moderately soluble in boiling methanol or acetone.   It melted sharply at 221° C.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.63%.

Method II.   The procedure adopted for the preparation of 2 : 4-dimethyl-quinoline was followed except that 2-methyl-3-keto-*n*-butanol was reacted with aniline (25 gm.), nitrobenzene (17 gm.) sulphuric acid (30 cc.) and ferrous sulphate (10 gm.).   There was obtained 18 gm. of a colourless distillate that crystallized almost completely on cooling.   After two recrystallizations from hexane it melted sharply at 74° C.   The picrate prepared from this melted before and after recrystallization at 221° C., and in admixture with that prepared as described above it melted at the same temperature.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.35%.

γ,γ,γ-Trichloro-α-(3-methyl-4-quinolyl)-propene

A mixture of 3 : 4-dimethyl-quinoline and a slight excess of chloral hydrate was heated on the steam bath with a pellet of anhydrous zinc chloride.   In the course of 30 min. the mixture became solid.   It was ground in a mortar with cold methanol and the solid, after filtering and washing with methanol, was recrystallized from a large volume of the same solvent.   Colourless hard prisms of the trichloro-quinolyl-propene melting at 218° C. were thus obtained. Calc. for $C_{13}H_{10}NCl_3$: N, 4.89%.   Found: N, 4.75%.   The yield was nearly quantitative.

8-Nitro-3 : 5-dimethyl-quinoline

To a solution of 15 gm. of 3-amino-4-nitro-toluene in 44 cc. of concentrated hydrochloric acid cooled to 0° C. was slowly added 15 gm. of α-methylacrolein. The mixture was allowed to come to room temperature, and after 30 min., 9 gm. of zinc chloride was added and the whole boiled under reflux for five hours.   The cooled solution was filtered to remove gums and basified with sodium hydroxide.   The precipitated base was filtered off, dried, and distilled

in vacuo. The crystalline distillate was recrystallized from methanol; it yielded 114 mg. of virtually colourless crystals of 8-nitro-3 : 5-dimethyl-quinoline melting at 192° C. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.85%. Found: N, 13.69%.

An attempt to prepare the same quinoline by using the Skraup conditions, but substituting α-methylacrolein for glycerol, gave the same substance. The yield was about the same as in the modified Doebner and v. Miller conditions described above.

8-Amino-3 : 5-dimethyl-quinoline

A solution of 150 mg. of 8-nitro-3 : 5-dimethyl-quinoline in 3 cc. of ethanol containing 0.1 cc. of hydrochloric acid was treated with 116 mg. of iron powder and boiled for 2.5 hr. The mixture was filtered and the insoluble residue washed with alcohol. The filtrate was evaporated somewhat, basified with sodium hydroxide, and extracted with ether. The alcohol insoluble residue was dissolved in dilute acid, the solution basified, and extracted with ether. The two ether extracts were combined, the solvent was removed, and the residue distilled *in vacuo.* There was obtained 93 mg. of an almost colourless crystalline distillate. A small portion was converted into its picrate, which, when recrystallized from methanol, melted at 214° C. Calc. for $C_{17}H_{15}O_7N_5$: N, 17.45%. Found: N, 17.36%.

3 : 5-Dimethyl-quinoline

The 8-amino derivative of this quinoline was diazotized and the diazo solution treated with an excess of hypophosphorous acid. After it had remained for about 15 hr. in the ice chest the solution was made alkaline and distilled in a current of steam. The colourless oil yielded a picrate which was moderately soluble in hot acetone or methanol. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.60%.

3 : 6-Dimethyl-quinoline

This base was prepared by the procedure outlined in the case of the 3 : 7-compound except that p-nitro-toluene was used instead of o-nitrophenol as the oxidizing agent. From 38 gm. of p-toluidine there was obtained 6.5 gm. of colourless crystalline base, which, when recrystallized twice from hexane, melted sharply at 58° C. Calc. for $C_{11}H_{11}N$: C, 84.08; H, 7.00%. Found: C, 84.10, 84.30; H, 6.76, 6.90%.

The picrate was rather sparingly soluble in hot methanol or acetone. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.53%.

3 : 7-Dimethyl-quinoline

In this preparation the writers were interested not only in obtaining the 3 : 7-base but also in isolating the small amount of accompanying 3 : 5-compound. Attempts to isolate pure 2 : 5-dimethyl-quinoline from the more abundant 2 : 7-dimethyl-quinoline formed in the Doebner and v. Miller synthesis of the latter from m-toluidine were only partially successful. A completely pure picrate could not be isolated by fractional crystallization.

This failure is attributed to the fact that we used a commercial specimen of *m*-toluidine that may have contained small amounts of the *o*- and *p*-isomers, and in consequence the bases in the mother liquor probably consisted of no fewer than four quinolines.   In order therefore to be certain of the purity of the *m*-toluidine it was prepared from 3-nitro-4-amino-toluene by first eliminating the amino group and then reducing the *m*-nitro-toluene.   The writers took the added precaution of distilling both the nitro compound and the toluidine through a Widmer column, arbitrarily discarding liberal amounts of end fractions.

To a mixture of 40 gm. of ferrous sulphate, 101 gm. of *m*-toluidine, 47 gm. of *o*-nitrophenol, and 105 cc. of sulphuric acid maintained at 140° C. was added 87 gm. of α-methylacrolein in the course of about 10 minutes.   It was then heated under reflux for 3.5 hr., diluted with water, and distilled in a current of steam to remove the excess *o*-nitrophenol.   The basified solution (sodium hydroxide) was again distilled with steam and the volatile base purified as in the case of the 7-ethyl-quinoline.   There was obtained 50 gm. of a pale greenish distillate that crystallized for the greater part, b.p. 101 to 103° (1 mm.)   The oil was drained off and the solid recrystallized twice from purified hexane.   It was obtained in colourless stout prisms melting sharply at 80° C.   Calc. for $C_{11}H_{11}N$:   C, 84.08; H, 7.00%.   Found: C, 84.05; H. 6.92%.

The picrate, prepared from the recrystallized 3 : 7-dimethyl-quinoline, was only sparingly soluble even in boiling acetone.   Calc. for $C_{17}H_{14}O_7N_4$:   N, 14.51%.   Found: N, 14.51%.

The oily mixture from which the crystalline base had crystallized was redistilled, cooled in the ice chest, and the oil drained from the crystals on a fritted glass filter.   Owing to the fact that the picrate of 3 : 5-dimethyl-quinoline is more soluble in methanol and in acetone than that of the 3 : 7-isomer. it was attempted to eliminate the latter by fractional precipitation. A certain amount of separation was accomplished but the picrate from the more soluble fractions melted indefinitely at 210° C. after repeated recrystallization.   That it consisted largely of the 3 : 5-compound was shown by the fact that in admixture with the pure 3 : 5-picrate it was completely liquid only at 215° C.

While searching for other derivatives suitable for separating these bases the writers observed that the perchlorate of 3 : 7-dimethyl-quinoline crystallizes rather well but is quite soluble even in cold water.   The bases were therefore recovered from their picrates and dissolved in hot dilute perchloric acid. Even while the mixture was still warm a sparingly soluble perchlorate crystallized from the solution.   This was filtered off (the quinoline regenerated from the filtrate crystallized at once; after pressing out on filter paper it melted at 78° C. and in admixture with 3 : 7-dimethyl-quinoline it melted at 79°C.), washed with cold water, and recrystallized from boiling water in which it is readily soluble.   The brilliant colourless prisms obtained by filtering,

washing, and drying melted sharply at 216° C.   Calc. for $C_{11}H_{11}N \cdot HClO_4$: N, 5.44%.   Found: N, 5.40%.

The base regenerated from the perchlorate was distilled *in vacuo* and obtained as a brilliantly colourless liquid that set to a glass on cooling to −80° C. When this was allowed to come to room temperature there was a temporary appearance of crystals at the junction between the glassy solid and the liquid base.   The picrate prepared in methanol from this base melted sharply at 220° C. either alone or in admixture with the picrate of the authentic specimen of 3 : 5-dimethyl-quinoline.   Recrystallization failed to raise this melting point.

The yield of pure base was almost 5 gm.   Since the separation was not entirely quantitative it is reasonable to assume that the 3 : 5-isomer constituted about 10 to 12% of the total mixture.

m-Toluidine

A mixture of 350 cc. of hydrochloric acid in one litre of water and 228 gm. of 4-amino-3-nitro-toluene was diazotized at 10 to 13° C. with a solution of 105 gm. of sodium nitrite in 450 cc. of water.   The excess of nitrous acid was removed by the addition of sulphamic acid and the solution was then treated with 250 gm. of 30% hypophosphorous acid cooled to 0° C.   This amount of hypophosphorous acid is much less than that used by Mai (14) or by Adams and Kornblum (1), but in our experience the yields are not increased by augmenting the quantity of acid.   The cold mixture was allowed to come to room temperature in the course of six hours, allowed to remain overnight, and distilled in a current of steam.   The *m*-nitro-toluene was extracted with benzene, washed with 10% sodium hydroxide solution, and the solvent removed.   The residual oil, which weighed 164 gm., was slowly distilled *in vacuo* through a Widmer column.   Copious end fractions were discarded.   The fraction boiling at 57° C. (1 mm.) weighed 143 gm. (70% yield).

The amine was prepared from this by reduction with iron filings and acetic acid.   It was also purified by slow distillation through a Widmer column.

3 : 8-Dimethyl-quinoline

This base was prepared by the procedure used for the 3 : 7-compound except that *o*-nitro-toluene was used as the oxidizing agent.   The yield was 10 gm. of twice distilled base from 38 gm. of *o*-toluidine.   It crystallized on chilling in ice but was liquid at room temperature.   Calc. for $C_{11}H_{11}N$: C, 84.08; H, 7.00%.   Found: C, 84.17; H, 7.28%.

The picrate was moderately soluble in boiling methanol or acetone.   Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%.   Found: N, 14.64%.

3 : 4 : 7-Trimethyl-quinoline

The procedure adopted for the preparation of the 3 : 4-dimethyl-quinoline gave such good yields of otherwise difficultly accessible quinolines that its applicability to other amines was tested.   There was also the possibility of

eliminating the 4-methyl group and thus obtain a variety of 3-methyl-quino-lines. These were ultimately obtained by a direct route so that the more involved procedure was abandoned. When molecular equivalents of *m*-toluidine (28 gm.) and *m*-nitro-toluene were substituted for the aniline and the nitrobenzene there was obtained 12 gm. of a colourless oil which crystallized for the greater part. The oil was removed on porous plate and the base recrystallized twice from hexane. It melted sharply at 78° C. Calc. for $C_{12}H_{13}N$: N, 8.10%. Found: N, 7.98%.

The picrate, prepared from the purified quinoline, melted sharply at 229° C. either before or after recrystallization from acetone-methanol. Calc. for $C_{18}H_{16}O_7N_4$: N, 14.00%. Found: N, 14.14, 14.12%. The styphnate and the trinitro-*m*-cresolate melted at 234° C. and 218° C. respectively.

3-Methyl-6-bromo-quinoline and its Debromination

The reactants and conditions for synthesizing this bromo-quinoline were the same as those used for the preparation of 3 : 7-dimethyl-quinoline except that *p*-bromo-aniline was substituted for *m*-toluidine. From 30 gm. of the aniline there was obtained 5 gm. of colourless fine needles of 3-methyl-6-bromo-quinoline, which, when recrystallized from hexane, melted at 103° C. Calc. for $C_{10}H_8NBr$: C, 54.05; H, 3.60; N, 6.31%. Found: C, 54.55; H, 3.67; N, 5.94%. The picrate was only very sparingly soluble in hot methanol, and it melted at 235° C. Calc. for $C_{16}H_{11}O_7N_4Br$: N, 12.42%. Found: N, 11.62%.

The bromo-quinoline (2.2 gm.) in ethanol (25 cc.) was boiled under reflux for three hours with 8 gm. of zinc-copper couple and sodium hydroxide (3 gm.) in a little water. The mixture was then distilled in a current of steam, the quinoline in the distillate extracted with benzene, and ultimately distilled *in vacuo*. The fraction boiling below 95° C. (1 mm.) yielded an orange coloured picrate of indefinite melting point. It was therefore heated with palladium–barium-sulphate in an atmosphere of hydrogen (200° C. for three hours). The product was redistilled to yield about 0.15 gm. of a colourless oil that gave a pure yellow picrate melting at 189° C. In admixture with an authentic specimen of 3-methyl-quinoline picrate it also melted at the same temperature.

4-Methyl-quinoline (Lepidine)

The synthesis of carbostyrils by the method of Knorr (13) gave good yields if the intermediate aceto-acetanilide was obtained in a state of moderate purity. It is frequently advantageous to dissolve the reaction product of ethyl acetoacetate and the aniline in ether and wash with dilute hydrochloric acid. Removal of the ether yields an oil that crystallizes readily. The solid may then be washed with a little petroleum ether. From 192 gm. of *p*-toluidine and 240 gm. of ethyl acetoacetate there was obtained 190 gm. of pure acetoacet-*p*-toluidide.

The conversion of the carbostyril into the corresponding quinoline by heating with zinc dust in an atmosphere of hydrogen (9) is not as satisfactory as the procedure of Mikhailov (16) who first converted the carbostyril into

the 2-chloroquinoline by means of phosphorus oxychloride and reduced this with tin and hydrochloric acid. By this method there was obtained 25 gm. of twice distilled lepidine from 58 gm. of 4-methyl-carbostyril. There is the possibility that the reduction with tin and hydrochloric acid may lead to the formation of tetrahydroquinolines. These, however, yield orange coloured picrates and with nitric acid they give an immediate intense blood red colour. None of the 4-methyl-quinolines gave either test. It is probable that the zinc dust procedure may result in the elimination or wandering of methyl groups. Otherwise it is difficult to account for the low melting points recorded by Ewins and King (9).

4 : 6-Dimethyl-quinoline

Reduction of 54 gm. of 4 : 6 dimethyl-2-chloroquinoline with 33.5 gm. of tin and 250 cc. of concentrated hydrochloric acid in 335 cc. of water yielded 27 gm. of pure 4 : 6-dimethyl-quinoline. Ewins and King give m.p. 230° C. (? corr.) for the picrate. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.62, 14.44%.

4 : 7-Dimethyl-quinoline

Owing to the possibility of also obtaining a small amount of 4 : 5-dimethyl-quinoline in this synthesis the intermediate 2-chloro-quinoline was distilled a second time. From 96 gm. of *m*-toluidine there was obtained 12 gm. of three times distilled 4 : 7-dimethyl-quinoline. The picrate was analysed. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.46%.

4 : 8-Dimethyl-quinoline

From 192 gm. of *o*-toluidine 35 gm. of the purified quinoline was obtained. Although this quinoline did not crystallize when placed in the ice chest it ultimately crystallized at room temperature. A small amount of oil was removed by pressing out on filter paper. The recrystallized base melted sharply at 58° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 8.91%. The picrate obtained in brilliant plates was moderately soluble in boiling methanol. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.50%.

4 : 5-Dimethyl-quinoline
  Method I

The 3-amino-4-methoxy-toluene was obtained by reducing 3-nitro-4-methoxy-toluene with iron and hydrochloric acid. The amino compound (27.1 gm.) was condensed with ethyl acetoacetate (30 gm.) (9) and the crystalline acetoacet-3-methyl-6-methoxy-anilide (38 gm.) recrystallized from ether-hexane; m.p. 81° C. Calc. for $C_{12}H_{15}O_3N$: N, 6.33%. Found: N, 6.26%. Ring closure was effected in sulphuric acid by the method of Mikhailov (16). The 2-hydroxy-8-methoxy-4 : 5-dimethyl-quinoline, obtained in 86% yield, was recrystallized from aqueous methanol, giving colourless glistening needles that melted at 219° C. Calc. for $C_{12}H_{13}O_2N$: N, 6.89% Found: N, 6.82%.

Elimination of both the hydroxyl- and the methoxyl-groups proved to be very wasteful. It was achieved in one step by distillation over zinc dust in a current of hydrogen at a temperature of 440° C. There was obtained 18 gm. of crude distillate from 52 gm. of carbostyril. The product was distilled, yielding 9.5 gm. of oil boiling at 165 to 180° C. (10 mm.). The distillate was dissolved in ether, washed with aqueous sodium hydroxide, and the recovered oil redistilled. The fraction boiling at 125 to 130° (3 mm.) was converted into its picrate, which was systematically recrystallized from acetone-methanol until it melted not quite sharply at 225° C. The quinoline was regenerated from this picrate and distilled. The fraction that distilled at 85 to 90° (1 mm.) crystallized on cooling. It was pressed out on filter paper and recrystallized from hexane. The colourless plates thus obtained melted at 76 to 77° C. The picrate prepared from this product was only sparingly soluble, and it melted at 233° C. Calc. for $C_{17}H_{14}O_7N_4$: N, 14.51%. Found: N, 14.53%.

Method II

The condensation of 3-amino-4-nitro-toluene (22 gm.) with 3-keto-*n*-butanol (20 gm.) under the conditions of the Doebner and von Miller synthesis was carried out by the Mills, Harris, and Lambourne (17) procedure. The cooled, diluted, and filtered reaction mixture was basified with an excess of sodium hydroxide. The precipitated base was filtered off, washed, dried, and distilled *in vacuo*. The reddish coloured oil, boiling at 170 to 180° C. (2 mm.), weighed 4.16 gm.; it crystallized on cooling. It was recrystallized from boiling methanol and the 8-nitro-4 : 5-dimethyl-quinoline thus obtained consisted of colourless needles melting at 140° C. Calc. for $C_{11}H_{10}O_2N_2$: N, 13.86%. Found: N, 14.01%.

The nitro compound was reduced with iron and dilute hydrochloric acid. The amino-quinoline was distilled (b.p. 125° C. (1 mm.)) and recrystallized from ether to yield colorless prisms that melted at 97° C. Calc. for $C_{11}H_{12}N_2$: N, 16.28%. Found: N, 16.47, 16.46%.

The above 8-amino-4 : 5-dimethyl-quinoline was converted into 4 : 5-dimethyl-quinoline by the procedure already described for the elimination of the amino group from other 8-amino-quinolines. In this case, however, the reaction did not proceed in a very satisfactory manner. During the diazotization an insoluble brown substance was precipitated and this did not yield 4 : 5-dimethyl-quinoline on treatment with hypophosphorous acid. The distilled quinoline, obtained in 6% yield, crystallized readily on cooling. When recrystallized from hexane it melted at 71 to 72° C. and in admixture with the base obtained as described above there was no melting below 72° C. The picrate prepared from this melted at 230° C. either alone or in admixture with the above picrate.

For final purification the combined 4 : 5-dimethyl-quinoline from the two sources was recrystallized again from hexane. The colourless plates thus obtained melted sharply at 78° C. Calc. for $C_{11}H_{11}N$: N, 8.92%. Found: N, 8.65%. The picrate was recrystallized twice more from acetone-methanol and it then melted at 233° C.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

II. SOME DEGRADATION EXPERIMENTS WITH LYCOPODINE[1]

By Léo Marion[2] and Richard H. F. Manske[2]

Abstract

The dehydrogenation of lycopodine with selenium has yielded a mixture of five bases, two of which have been identified as 7-methyl-quinoline and 5 : 7-dimethyl-quinoline respectively. Heating the alkaloid with palladium on barium sulphate or with phthalic anhydride also yields 7-methyl-quinoline. It is concluded that the quinoline nucleus, completely hydrogenated, is present as such in lycopodine. The oxygen may be present as a cyclic ether.

The alkaloid lycopodine is the major basic constituent of a number of *Lycopodium* species now under investigation (2). Achmatowicz and Uzieblo (1) have assigned the formula $C_{16}H_{25}ON$ (which we have confirmed) to lycopodine and shown that methoxyl and N-methyl groups are absent as well as active hydrogen (Zerewetinoff). It is therefore probable that the nitrogen is common to two rings and that the oxygen is present either in a ketonic group or in a cyclic ether.

After treatment with phenyl-magnesium bromide at 100° C., lycopodine was recovered quantitatively. It could not be hydrogenated at 200° in butanol over Raney nickel at 2000 lb. per sq. in. These results seem to indicate that there is no ketonic group in lycopodine and that the oxygen is probably present in a cyclic ether linkage. Treatment of the alkaloid with hydrogen iodide and red phosphorus gave some confirmation of this supposition. There was obtained an amorphous base that contained iodine and slowly polymerized to an insoluble resin.

The dehydrogenation of the alkaloid with selenium yielded a complex mixture from which it was possible to isolate five bases as their picrates. Two of these have been identified as 7-methyl-quinoline and 5 : 7-dimethyl-quinoline respectively.

The formation of quinolines as the result of the high temperature decomposition of an alkaloid cannot be regarded as positive proof of the presence of the quinoline skeleton. The history of the chemistry of cytisine is ample warning that such assumptions may be premature. Nevertheless, 7-methyl-quinoline was obtained from lycopodine in two other ways, which from the nature of the reagents employed would not be expected to bring about the same change if this depended upon the opening and subsequent re-forming of rings. In the one experiment the alkaloid was heated in an atmosphere of nitrogen with palladium–barium-sulphate and in the other it was heated

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with phthalic anhydride in an evacuated tube.   It is therefore assumed that the quinoline nucleus, completely hydrogenated, is present as such in lyco-podine.

Experimental

Degradation of Lycopodine with Selenium

Lycopodine (2 gm.) was mixed with black selenium (2 gm.) in a small flask carrying a column about 60 cm. long, at the top of which a side arm was con-nected to a downward condenser.   A slow stream of nitrogen was kept sweeping into the flask through a capillary tube extending down the column. After the air had been displaced, the flask was dipped into a metal bath and, in the course of two hours, the temperature was raised gradually to 310° C. and kept at that temperature for one-half hour.   Two more runs, each with 2 gm. of base, were made in exactly the same way.

The distillates were collected in ether and combined with the ether soluble portion obtained from the residues.   The resulting ether solution was extracted repeatedly with small quantities of dilute hydrochloric acid, washed with water, and dried over sodium hydroxide.   The ether was distilled off and the residual neutral oil (1.5 gm.) distilled *in vacuo*, b.p. 135 to 140° C. (2 mm.). This oil, although it contains no nitrogen, nevertheless gave a red colour with Ehrlich's reagent not unlike that given by indoles.

The residues from the selenium treatment which had been extracted with ether were repeatedly digested with methanol containing a little hydrochloric acid.   The combined acid extracts were diluted with water, evaporated on the steam-bath to remove the methanol and the residue dissolved in water. After filtration through charcoal, the aqueous solution was combined with the acid extract obtained from the distillates.

Isolation of 7-Methyl-quinoline and 5 : 7-Dimethyl-quinoline

The combined acid solution was extracted with ether (discarded), basified, with strong sodium hydroxide and the precipitated base collected in ether. The ether solution was washed with water, dried over anhydrous potassium carbonate, and evaporated on the steam-bath.   The residual dark oil (3 gm.) was fractionated *in vacuo*: fraction I, colourless oil, b.p. 80 to 90° C. (2 mm.); fraction II, colourless oil, b.p. 130 to 140° (2 mm.); fraction III, yellow oil, b.p. 170 to 180° (2 mm.); fraction IV, thick, light-brown oil, b.p. 185 to 210° (2 mm.); fraction V, an undistilled residue weighing a little less than half the combined distillates.

Fraction I was dissolved in methanol and added to a boiling solution of picric acid in methanol.   The picrate, which separated in yellow needles, was recrystallized several times from methanol.   The free base was regenerated, distilled (b.p. 75 to 80° C. (2 mm.), small end fractions being discarded), and reconverted to the picrate, m.p. 242°.   Admixture with an authentic specimen of 7-methyl-quinoline picrate failed to depress the melting point.   Calc. for $C_{16}H_{12}O_7N_4$: C, 51.69; H, 3.22; N, 15.05%.   Found: C, 52.29; H, 3.62; N, 15.69%.   The styphnate melted at 242° either alone or in admixture with

an authentic specimen of 7-methyl-quinoline styphnate.   The mother liquor of the first crystallization of 7-methyl-quinoline picrate was concentrated and, on cooling, it yielded a second, more soluble, picrate which, after one recrystallization, melted at 167°.   Calc. for $C_{17}H_{18}O_7N_4$: C, 52.30; H, 4.62; N, 14.35%.   Found: C, 52.15; H, 4.73; N, 14.69%.

Fraction II formed a picrate which, after several recrystallizations from acetone–methanol, melted at 246° C. and in admixture with 5 : 7-dimethyl-quinoline picrate melting at 249° (3) it melted at 248°.   Calc. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.62; N, 14.51%.   Found: C, 52.82; H, 3.83; N, 14.55%.

Fraction III also formed a picrate which, after two recrystallizations from boiling methanol, melted at 169° C.   Calc. for $C_{22}H_{22}O_8N_4$: C, 56.17; H, 4.68; N, 11.91%.   Found: C, 55.66; H, 4.60; N, 11.90%.   The mother liquor from this picrate, when further concentrated yielded a more soluble picrate, m.p. 151°.   Calc. for $C_{22}H_{24}O_7N_4$: C, 57.90; H, 5.26; N, 12.28%.   Found: C, 58.01; H, 5.12; N, 12.83%.

Fraction IV, after refractionation, yielded an oil from which the same picrate (m.p. 169° C.) was obtained as from fraction III.

The undistilled residue (fraction V) was distilled under a pressure of 10^{-3} mm. but the various fractions obtained failed to yield crystalline picrates. There was present an appreciable amount of combined selenium in these fractions.

Dehydrogenation of Lycopodine

Lycopodine (about 0.5 gm.) was mixed with palladium–barium-sulphate (about 0.5 gm.) and the mixture heated in an oil bath in an atmosphere of nitrogen for seven hours at 250° C.   The reaction mixture was allowed to cool and was distilled *in vacuo*.   It yielded fraction I, colourless oil, b.p. 105 to 110° (1.5 mm.) and fraction II, thick, yellow oil, b.p. 130 to 150° (1.5 mm.).

Fraction I formed a picrate consisting of pale yellow needles, m.p. 242° C. Admixture with 7-methyl-quinoline picrate failed to depress the melting point. After concentration of the mother liquor there separated an oily picrate from which the base was liberated.   This base yielded a crystalline perchlorate which, after repeated recrystallization from methanol, melted at 285°.   This seems to be identical with the perchlorate obtained similarly from the product of the reaction of lycopodine with phthalic anhydride described below.   The amount of material on hand, however, did not permit further comparison nor an analysis.

Reaction of Lycopodine with Phthalic Anhydride

Lycopodine (1 gm.) was mixed with phthalic anhydride (1 gm.), and the mixture was sealed into an evacuated tube and heated in an oil bath for seven hours at 250° C.   The resulting black resin was repeatedly extracted with small quantities of hot dilute hydrochloric acid.   The combined acid solution was filtered through charcoal, basified with strong sodium hydroxide, and extracted with ether.   The ether solution was distilled on the steam-bath to remove the solvent and the residual oil fractionated *in vacuo*: fraction I,

b.p. 100 to 110° (2 mm.) and fraction II, b.p. 130 to 145° (2 mm.).   The first fraction yielded a picrate identified by melting point and mixed melting point as 7-methyl-quinoline picrate.   The mother liquor from this picrate, when concentrated, deposited an oily picrate from which a base was liberated. This base formed a perchlorate crystallizable from methanol, m.p. 285°. Calc. for $C_{14}H_{23}N \cdot HClO_4$: C, 55.00; H, 7.86; N, 4.58%.   Found: C, 54.81; H, 8.10; N, 4.35%.

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